

CHAPTER IV

BLEND OF NYLON 6/HDPE WITH MAH-GHDPE COMPATIBILIZER: STUDY NEUTRALIZATION OF MALEIC ANHYDRIDE GROUP BY ZINC ACETATE DIHYDRATE EFFECT ON COMPATIBILITY OF BLEND

4.1 Abstract

Blends of Nylon 6 (polyamide-6) and HDPE (high-density polyethylene) with blend ratios of 80/20 (wt/wt) and 20/80 (wt/wt) were studied using zinc-neutralized maleic anhydride grafted HDPE (MAH-gHDPE) as compatibilizers. Maleic anhydride groups were hydrolyzed and neutralized with different amounts of zinc acetate dihydrate in a twin-screw extruder to produce different levels of zinc-neutralization (0, 25, 50, 75, and 100 %) at one and ten parts per hundred of resin of compatibilizer. SEM micrographs showed a large reduction in the dispersion phase size in the compatibilized blends. Tensile measurements showed improvement of tensile strength for all compatibilized blends; moreover, the elongation at break of compatibilized blends at 10 phr of compatibilizer was improved. Blending increased the crystallization temperature for the Nylon 6, and the addition of compatibilizer reduced the crystallization temperature slightly. A significant increase in melt viscosity of the compatibilizer was found with zinc addition and adding compatibilizer increased the viscosity of the blends. However, the addition of zinc to the compatibilizer did not change the viscosity in the Nylon 6 rich blends and actually led to a decrease in viscosity in the HDPE-rich blends.

Keywords: High-density polyethylene, Nylon 6, Maleic anhydride grafted high-density polyethylene, Compatibilizers, Blends

4.2 Introduction

High performance properties of materials; for example chemical resistance, low water absorption, high strength, high impact resistance, and barrier properties, are required for specialized applications. A simple process to produce a new material is by blending two or more polymers. Polyamide-6/High-density polyethylene (Nylon 6/HDPE) blends have been widely investigated. Nylon 6 shows high tensile strength and has good barrier properties, while HDPE shows good impact resistance, and good low temperature flexibility. Nylon 6/HDPE blends are thermodynamically immiscible and generally have poor ultimate mechanical properties. When these immiscible blends are subjected to stress, the stress concentrates at the interfacial phase of immiscible blends which in turn tend to serve as failure initiation nuclei [1-5].

The properties of immiscible blends can be enhanced by adding a third component which is an interfacially active material termed a compatibilizer. Compatibilizers promote physical and/or chemical interactions between each polymer component. Frequently, polymeric materials based on derivatives of carboxylic acid groups are used as compatibilizers. In this case, compatibility of the blend is achieved by interactions of the carboxylic acid and the active functional group of one or both of the polymers.

Many kinds of acid-functionalized compounds have been proposed as compatibilizers for polyamide/polyolefins blends; for example, ethylene-methacrylic acid copolymer (E-MAA) [3, 4, 6], acrylic acid grafted polyethylene (PE-g-AA) [6-8], and maleic anhydride grafted polyethylene (MAH-gPE) [1, 9-17]. These compatibilizers promote reactions between amine groups (terminal $-NH_2$ or $-RNH$) of Nylon 6 with carboxylic acid functional groups and/or interactions between carboxylic acid groups and these polyamide functional groups [3, 4, 18-20].

The aim of this work was to study the effect of zinc-neutralization of hydrolyzed anhydride acid groups in MAH-gHDPE with respect to the efficiency of compatibilization. Zinc acetate dihydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$) was used as a neutralizing agent for the melt-neutralization reaction. Zinc acetate dihydrate rather than zinc oxide [21] as was done in our previous work was employed to see if there

were any significant differences in behavior between the two neutralizing agents. Zinc oxide is used commercially to neutralize similar materials (e.g. ethylene methacrylic acid) because of cost; however, the acetate might neutralize differently because the neutralization chemistry is more straightforward and the acetic acid byproduct of the acetate should evaporate during melt neutralization. Characterization of phase morphology, mechanical properties, thermal properties, and rheological properties of the obtained Nylon 6/HDPE blends with and without MAH-gHDPE and zinc neutralization of MAH-gHDPE have been carried out.

4.3 Experimental

4.3.1 Materials

Nylon 6 (polyamide-6) employed in this study was an injection-molding grade (1013B), supplied by UBE Nylon (Thailand). High-density polyethylene (HDPE) was also an injection-molding grade (H5480S) supplied by Thai Polyethylene Co., Ltd. (TPE). Maleic anhydride grafted on high-density polyethylene (MAH-gHDPE) produced by DupontTM, USA, under the trademark FusabondTM E MB 100D (0.9 wt% maleic anhydride (MAH) grafted level was determined by acid-base titration procedure), was supplied by Creative Polymer Co., Ltd., Thailand. Finally, zinc acetate dihydrate was obtained from Ajax Finechem.

4.3.2 Zinc-neutralization of Maleic Anhydride Grafted on High-density Polyethylene

The required amount of MAH-gHDPE with zinc acetate dihydrate was dried and premixed in a tumble mixer for 10 min and then melt-neutralized in a twin-screw extruder (Collin D-8017 T-20) at 230°C and screw speed at 35 rpm. Levels of neutralization of MAH studied in this work were 10%, 25%, 50%, 75%, and 100% neutralization, and complete neutralization was assumed. The obtained materials were dried and kept in sealed plastic bags to prevent any contact with moisture. The neutralization reaction was confirmed by Fourier Transform Infrared Spectroscopy (FT-IR). FT-IR spectra of both unneutralized and neutralized MAH-gHDPE were obtained using a Nicolet Nexus 670 FT-IR spectrometer in the wavenumber range of

4000-400 cm^{-1} with 32 scans at a resolution of 2 cm^{-1} . A thin film sample for FT-IR was prepared by compression molding.

4.3.3 Blends and Sample Preparations

The required amount of HDPE, Nylon 6 and zinc-neutralized MAH-gHDPE were premixed in a tumble mixer for 10 min followed by drying in a vacuum oven at 60°C for 24 h. The materials were then blended in a Collin D-8017 T-20 twin-screw extruder with a screw speed of 35 rpm and temperature 230°C. The levels of compatibilizer used in these studies were 1 and 10 part per hundred of resin (phr). Test specimens were prepared using a WABASH V 50 H 50 ton compression molding machine. Blend samples were placed in a picture frame mold, and the mold was preheated at 250°C for 3 min in the press without applied force. The mold was then compressed under a force of 10 tons for a further 2 min, after which the mold was cooled to 40°C under applied force. Test specimens were cut from the molded sheets using a pneumatic punch machine.

4.3.4 Scanning Electron Microscopy (SEM)

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 xylene (for HDPE minor blends) and (ii) formic acid (for Nylon 6 minor blends). The specimens were then coated with gold under vacuum and all scanning electron micrographs were taken using 15 kV with at 1500x magnification. The number average diameter (d_{n_i}) of dispersion phase was evaluated by SEMAfore software, using equation (1):

$$d_{n_i} = \sum(n_i d_i) / n_i \quad (1)$$

where n_i is the number of droplet and d_{n_i} is the diameter of the i^{th} droplet.

4.3.5 Tensile Test

An Instron Universal tester was used to measure tensile properties of the blend samples using compressed specimens. Testing was carried out following the procedure outlined in ASTM D638-91 test procedure using a crosshead speed of 50 mm/min and a gauge length 50 mm.

4.3.6 Differential Scanning Calorimetry

Thermal analysis of blends was carried out on a Perkin-Elmer DSC 7. All scans were made under nitrogen atmosphere (N₂) to minimize oxidative degradation. Temperature calibration was obtained by measuring the melting temperature of indium element. 7-10 mg samples were placed in an aluminum pan and sealed. The sealed pans were heated from 30°C to 250°C at a heating rate of 80°C/min, and held at 250°C for 5 minutes to remove any thermal history and then cooled to 30°C at 10°C/min. The samples were then heated from 30°C to 250°C at 10°C/min. Crystallinity for each polymer component of the compatibilized blends was determined from knowledge of the ratio of the melting enthalpy for 100% crystallinity of pure components. The crystallinity of each component in the blend was calculated using Equation (2):

$$\chi_{c,i} = \frac{\Delta H_i}{\Delta H_{f,i} \times W_i} \times 100\% \quad (2)$$

where $\chi_{c,i}$ is the percent crystallinity for the i_{th} polymer component (polyamide or polyethylene), W_i is the weight fractional of polymer component in the blend, ΔH_i is the melting enthalpy of the component present in the blends, $\Delta H_{f,i}$ is the heat of fusion for the 100% crystallinity of the pure polymer component (190 J/g for Nylon 6, and 293 J/g for HDPE). Crystallization and melting temperatures were determined by the temperature corresponding to maximum heat flow.

4.3.7 Dynamic Mechanical Analysis (DMA)

Dynamic mechanical analyses (DMA) of the Nylon 6/HDPE blends were studied using a Solid Analyzer RSA II (Rheometric Scientific). The storage modulus (E') and loss modulus (E'') were measured as a function of temperature. The 3-point bend fixture was used to mount the samples and temperature step of 4 K intervals were used. All experiments were performed at 1 Hz frequency and 0.025% strain amplitude using static force tracing dynamic force.

4.3.8 Capillary Rheometer

A CEAST Rheologic 5000 Twin-bore Capillary Rheometer was used to evaluate melt-rheology of the zinc-neutralized MAH-gHDPE, neat Nylon 6, neat HDPE, and 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 ($L/D = 20$) and all measurements were operated at 240°C. The apparent viscosity of all the blends data were computed by VisualRHEO, a software based on CeastVIEW platform to be used with Rheologic and Smart RHEO instrument for process test evaluations.

4.4 Results and discussion

4.4.1 Melt Rheological Properties, FTIR Spectra and Thermal Properties of Zinc-neutralized MAH-gHDPE

Melt viscosity changes with zinc-neutralization in MAH-gHDPE as has been shown previously [20, 22, 23]. Figure 4.1 shows apparent shear viscosity vs. shear rate curves of MAH-gHDPE with different zinc levels. The apparent shear viscosity of zinc-neutralized MAH-gHDPE was higher than that of unneutralized MAH-gHDPE due to ionic crosslinking in the zinc-neutralized MAH-gHDPE chains. The apparent shear viscosity was maximum at 75% zinc-neutralization of MAH-gHDPE. Since the viscosity should be proportional to the number of crosslinks formed, this result suggests that the number of ionic crosslinks formed in the 75% case was higher than in the 100% case. There are two possibilities for such a reduction with a higher neutralization level: an increase in intrachain crosslinking vs.

interchain crosslinking, or an increase in the average size of ionic crosslinks (i.e. number of carboxylate ions per crosslink).

The interactions of zinc ions with MAH-gHDPE chains was studied with FTIR spectra from both neutralized (Figure 4.2b, 4.2c and 4.2d) and unneutralized MAH-gHDPE (Figure 4.2a). In Figure 4.2a, weak bands at 1793 and 1867 cm^{-1} observed in the FTIR spectrum correspond to symmetric and asymmetric stretching of C=O in the non-conjugated five member-ring of maleic anhydride [24, 25]. The peak at 1715 cm^{-1} refers to the hydrogen-bonding of carboxylic acid pairs, which resulted from hydrolysis of some maleic anhydride [25]. With increasing zinc-neutralization level, the characteristic peak of maleic anhydride at 1793 cm^{-1} is reduced and the characteristic peak at 1583 cm^{-1} (broad peak) belonging to zinc-carboxylate structures from neutralization of hydrolyzed maleic anhydride functional groups [24-26] was observed. At 100% neutralization, the two weak bands and the 1715 cm^{-1} band had disappeared with a large increase in the band at 1583 cm^{-1} and the clear emergence of a band at 1680 cm^{-1} (this same band may have been present at lower neutralization levels). We do not know the characteristic bond responsible for the appearance of this band; however free acetic acid does not have an IR band at this wavenumber.

Thermal properties of zinc-neutralized MAH-gHDPE from DSC experiments are shown in Table 4.1. Melting temperature (T_m) increased with neutralization level and was a maximum at 50% zinc-neutralization but the T_m of MAH-gHDPE at 75% and 100% zinc-neutralization dropped off and was almost equal to T_m of MAH-gHDPE. Although seemingly strange, 50% neutralization represents a unique combination of hydrogen and zinc-carboxylate bonding as described previously by our group based on small-angle x-ray scattering and x-ray absorption studies [27]. Crystallization temperature (T_c) of MAH-gHDPE decreased with zinc-neutralization level to 50% followed by no change at higher neutralization. Percent crystallinity (χ_c) of MAH-gHDPE also decreased with neutralization level with no change after 50% neutralization.

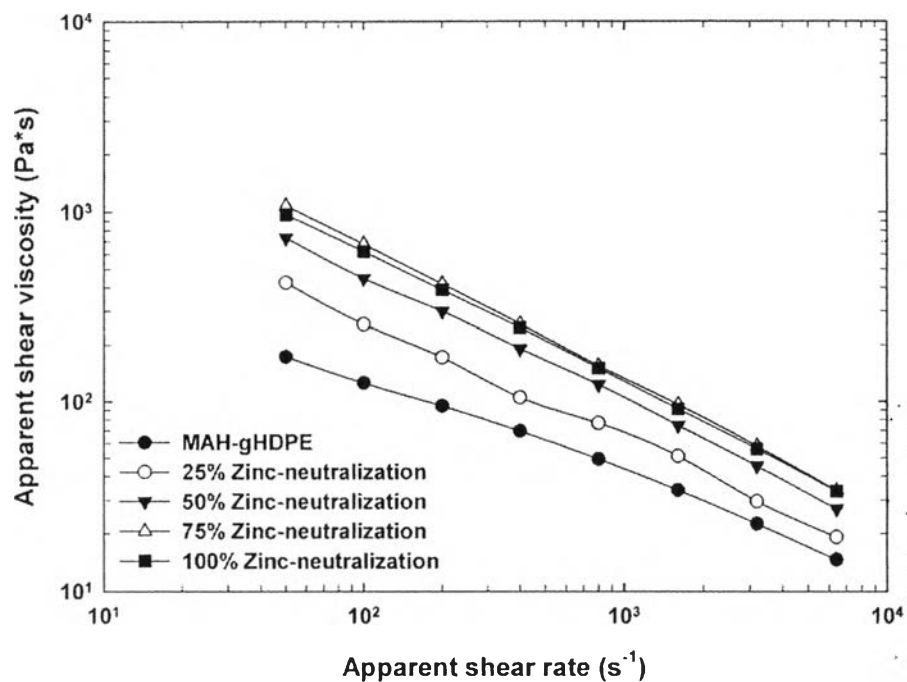


Figure 4.1 Apparent shear viscosity vs. apparent shear rate for zinc-neutralized MAH-gHDPE with neutralization levels indicated on chart

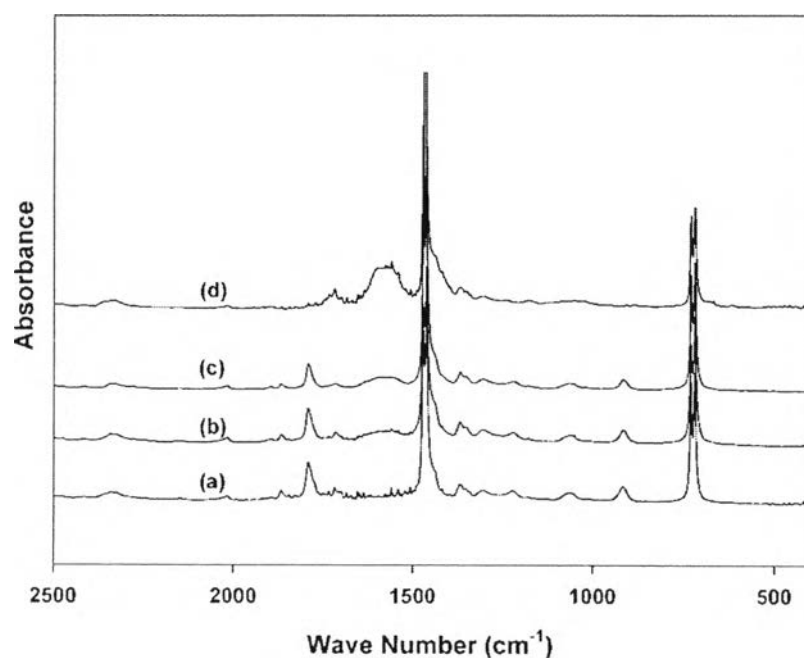


Figure 4.2 FT-IR spectra in range of 2500 to 400 cm^{-1} . (non-neutralized MAH-gHDPE (a), 25% (b), 50% (c), and 100% (d) zinc-neutralized MAH-gHDPE

Table 4.1 DSC experiment data for MAH-gHDPE and their zinc-neutralized MAH-gHDPE

% Zinc-neutralization	MAH-gHDPE		
	T_m (°C)	T_c (°C)	(χ_c)
0	129.94	116.27	58.40
25	132.54	114.60	56.01
50	134.21	110.27	47.94
75	130.02	111.39	48.88
100	130.62	111.31	47.92

4.4.2 Nylon 6/HDPE blends with MAH-gHDPE

4.4.2.1 *Morphologies of blends*

Figures 4.3 and 4.4 show SEM micrographs of both HDPE/Nylon 6 20/80 (Nylon 6 rich blend) and HDPE/Nylon 6 80/20 (HDPE rich blend) respectively with various MAH-gHDPEs as compatibilizers. Without compatibilizers (Figure 4.3a), the size of the minor phase was found to be 34 μm . All of the compatibilized blends showed dramatic decreases in dispersed phase sizes. Figures 4.5a and .45b show the number average of dispersed phase size of minor phase of both Nylon 6 rich blends and HDPE rich blends with different zinc-neutralization level MAH-gHDPE as compatibilizers. At a level of one phr, 25% and 50% zinc-neutralized MAH-gHDPE compatibilizer caused a larger reduction in dispersed phase size as opposed to the unneutralized compatibilizer for both blend compositions with a higher reduction for the HDPE-rich blend. When 10 phr of 0%, 25%, and 50% zinc-neutralized MAH-gHDPE compatibilizer was added, there was a further reduction in phase size of the minor phase, but at 10 phr the unneutralized material yielded the smallest dispersed phase. For both the Nylon 6 rich blend and HDPE-rich blend with 100% zinc-neutralized MAH-gHDPE, dispersed phase size was larger than blends made with unneutralized MAH-gHDPE compatibilizer. These observations are consistent with one theory of compatibilization in these materials: namely that compatibilization is caused by carboxylic acids reacting with the amine or amide groups of the polyamide with zinc serving as a catalyst. At 100% neutralization, there are no carboxylic acid groups present which in turn reduces the compatibilizer effect while at high compatibilizer levels, the catalytic effect is not

needed to get sufficient reaction and hence compatibilization is simply driven by the concentration of carboxylic acid groups.

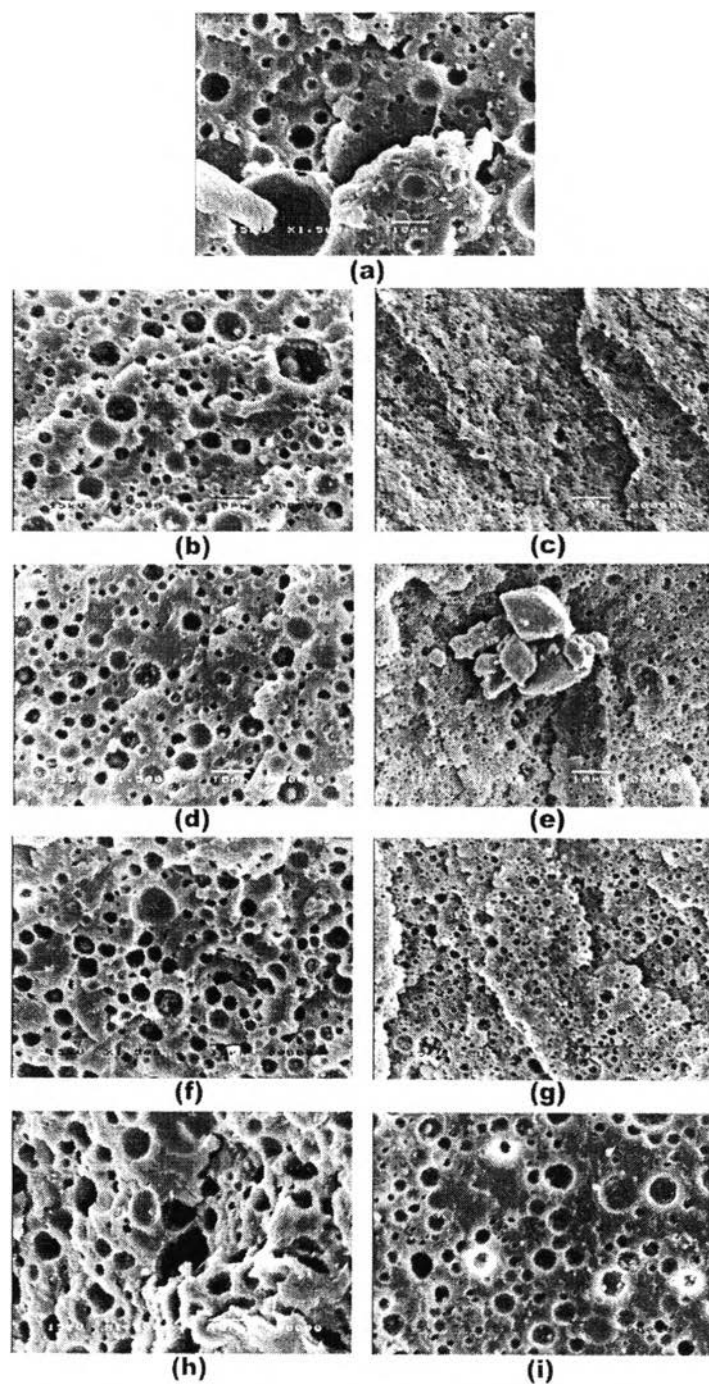


Figure 4.3 SEM micrographs of fractured morphologies for Nylon 6/HDPE: 80/20 blend (Nylon 6 rich blend); (a) uncompatibilized, 1 phr of (b) 0%, (d) 25%, (f) 50%, and (h) 100% zinc-neutralized MAH-gHDPE, and 10 phr of (c) 0%, (e) 25%, (g) 50%, and (i) 100% zinc-neutralized MAH-gHDPE

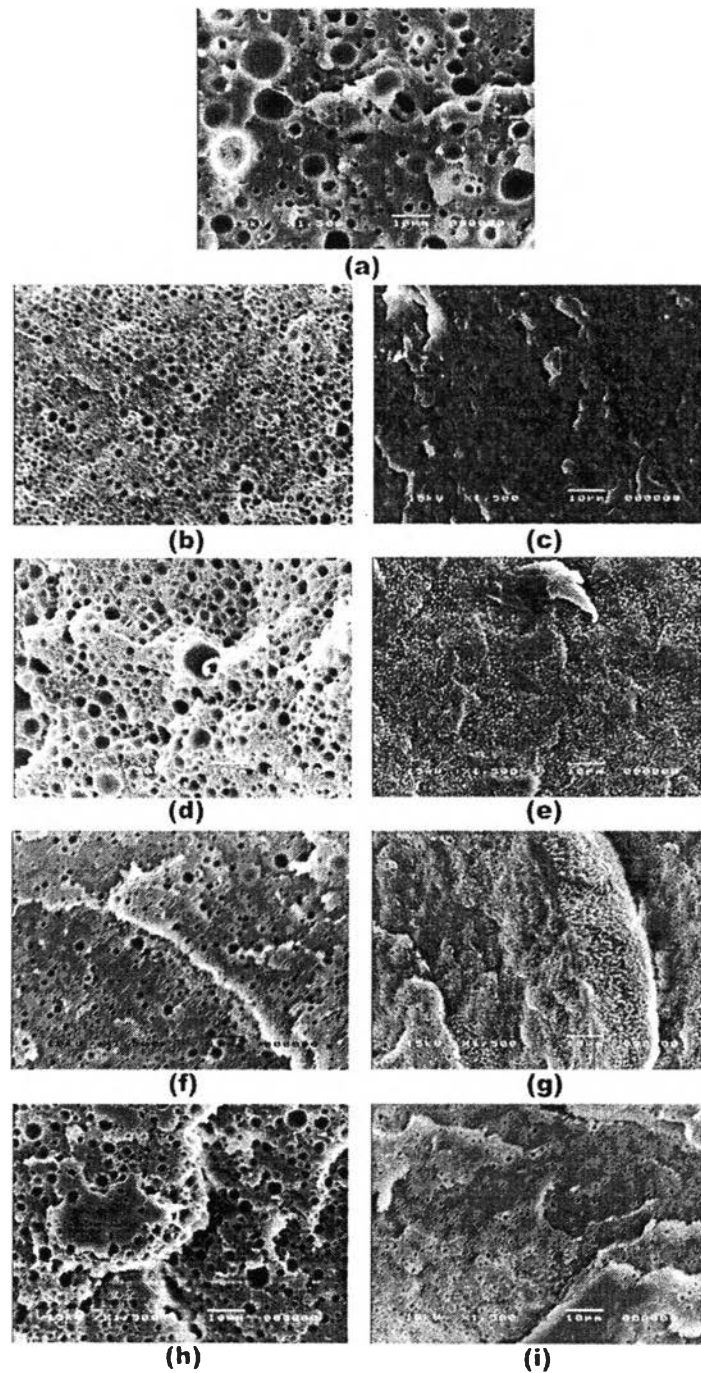


Figure 4.4 SEM micrographs of fractured morphologies for Nylon 6/HDPE: 20/80 blend (HDPE rich blend); (a) uncompatibilized, 1 phr of (b) 0%, (d) 25%, (f) 50%, and (h) 100% zinc-neutralized MAH-gHDPE, and 10 phr of (c) 0%, (e) 25%, (g) 50%, and (i) 100% zinc-neutralized MAH-gHDPE

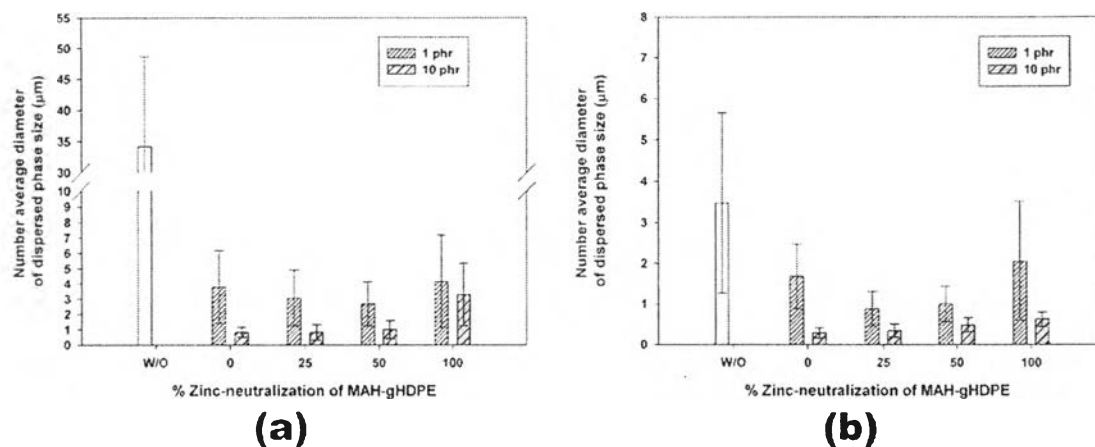


Figure 4.5 Number average particle diameter of dispersion phase size for (a) Nylon6 rich blend, and (b) HDPE-rich blend with different compatibilizers.

4.4.2.2 Tensile Properties

Figure 4.6 show tensile strength, tensile modulus, and % elongation at break of both Nylon 6 rich blends and HDPE-rich blends. All compatibilized blends show higher tensile strengths than the uncompatibilized blends, however the elongation at breaks were only higher for the 10 phr samples. Other striking results are the significant increases in elongation at break at 10 phr added compatibilizer vs 1 phr added compatibilizer, which is consistent with the reduction in phase size. At 100% neutralization there is a reduction in elongation as opposed to blends compatibilized with partially neutralized materials, which is consistent with the changes in dispersed phase size. Another observation is that the tensile strength drops for the Nylon 6 rich blend made with compatibilizer having 75% and 100% zinc neutralization, while such an effect is not apparent for the HDPE rich blend. Tensile moduli are basically unaffected by the addition of compatibilizer.

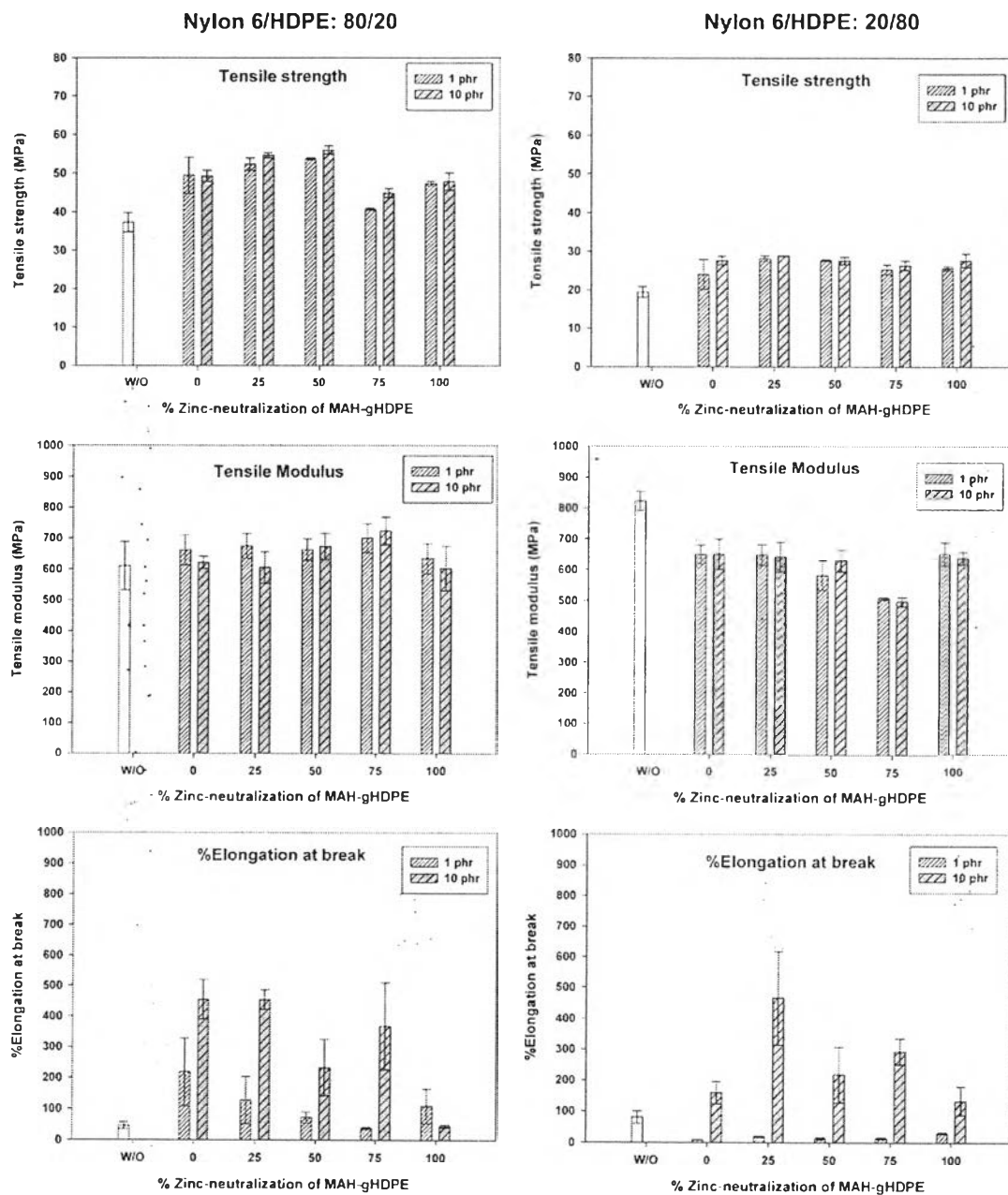


Figure 4.6 Tensile properties for Nylon 6 rich blend and HDPE rich blend with different compatibilizers.

4.4.2.3 Differential Scanning Calorimeter (DSC)

DSC was used for determined melting temperature (T_m), crystallization temperature (T_c) and % crystallinity (χ_c) with results shown in Table 4.2. Melting temperature (T_m) for the HDPE component clearly increases when blended with the polyamide for the HDPE rich blend, the increase is about 2°C and does not depend on whether a compatibilizer is present. In the Nylon 6 rich blend, no change was found in the T_m upon blending.

Nylon 6 crystallization temperatures were significantly higher in all cases upon blending. At 10 phr compatibilizer at low Nylon 6 contents, the crystallization temperature could not reliably be determined. The increases ranged from 2-4°C for the compatibilized blends, with no clear dependence on compatibilizer type or level. The highest crystallization temperature was found for the uncompatibilized Nylon 6 rich blend, an increase of nearly 5°C. These increases are clear evidence of nucleation by the polyethylene in the crystallization process; the reduction upon compatibilization is likely due to reduced chain diffusion caused by interfacial reactions [9, 15, 21]. An increase was also found for the HDPE upon blending, although the temperature change was smaller. In this case, the Nylon 6 rich blend with no compatibilizer had the smallest increase in T_c .

Percent crystallinity (χ_c) of the Nylon 6 decreased upon blending for the Nylon 6 rich blend. The higher compatibilizer level showed a smaller crystallinity, with no consistent effect of neutralization level on the crystallinity. The increase in polyethylene crystallinity as compared to unblended HDPE in the Nylon 6 rich blend was significant for the 10 phr material with no change at 1 phr compatibilizer. Uncompatibilized material had the smallest HDPE fractional crystallinity with a value 4% smaller than the pure HDPE. For the HDPE rich blend, the values for Nylon 6 had a high variability meaning that no conclusions could be made, while the HDPE fractional crystallinity was unaffected by blending.

Table 4.2 DSC experiment data for Nylon 6, HDPE and their blends

Blend systems	Amount of Compatibilizers (phr)	% Zinc-neutralization	Nylon 6			HDPE		
			T _m (°C)	T _c (°C)	(χ_c)	T _m (°C)	T _c (°C)	(χ_c)
Nylon 6	-	-	220.70	182.47	33.23	-	-	-
HDPE	-	-	-	-	-	131.2	113.63	60.78
80/20	-	-	221.20	187.30	30.13	131.03	113.80	56.42
80/20	1	0	220.37	185.97	29.99	130.53	114.13	57.78
80/20	1	25	220.37	185.97	36.46	130.53	114.13	61.04
80/20	1	50	220.70	185.80	29.61	131.20	114.47	58.94
80/20	1	75	221.70	186.63	32.94	131.37	115.30	62.30
80/20	1	100	220.87	185.63	29.19	130.53	114.63	56.23
80/20	10	0	220.53	183.13	27.88	129.87	114.47	75.28
80/20	10	25	220.03	182.97	27.41	129.20	114.80	75.94
80/20	10	50	221.73	184.97	27.77	129.53	114.97	71.28
80/20	10	75	221.87	186.47	27.33	131.20	115.63	73.88
80/20	10	100	221.37	185.30	28.36	131.20	114.80	76.27
20/80	-	-	220.53	185.97	29.11	133.20	114.47	60.22
20/80	1	0	220.53	185.47	29.11	133.20	114.47	59.42
20/80	1	25	220.53	185.63	29.06	132.87	114.47	62.09
20/80	1	50	220.70	185.97	21.62	133.53	114.13	63.08
20/80	1	75	220.53	186.47	33.87	132.53	115.13	60.55
20/80	1	100	220.87	186.63	28.81	132.37	114.80	59.97
20/80	10	0	219.70	-	30.14	133.37	115.13	62.04
20/80	10	25	220.85	-	31.19	133.03	114.97	62.96
20/80	10	50	220.70	-	34.37	132.53	115.13	60.13
20/80	10	75	221.03	-	35.95	133.87	115.97	64.01
20/80	10	100	221.53	-	32.43	132.70	114.80	60.38

4.4.2.4 Dynamic Mechanical Analysis (DMA)

DMA spectra of Nylon 6/HDPE blends with MAH-gHDPE and 100% zinc-neutralization of MAH-gHDPE compatibilizers are presented in Figure 4.7. No significant changes were seen in the spectra, as expected for the HDPE rich blend given that no change was found in HDPE crystallinity with blending. For the Nylon 6 rich phase material, a drop in modulus was expected upon blending given the drop in crystallinity of the major Nylon 6 phase, especially for the 10 phr compatibilized material, but no drop was found.

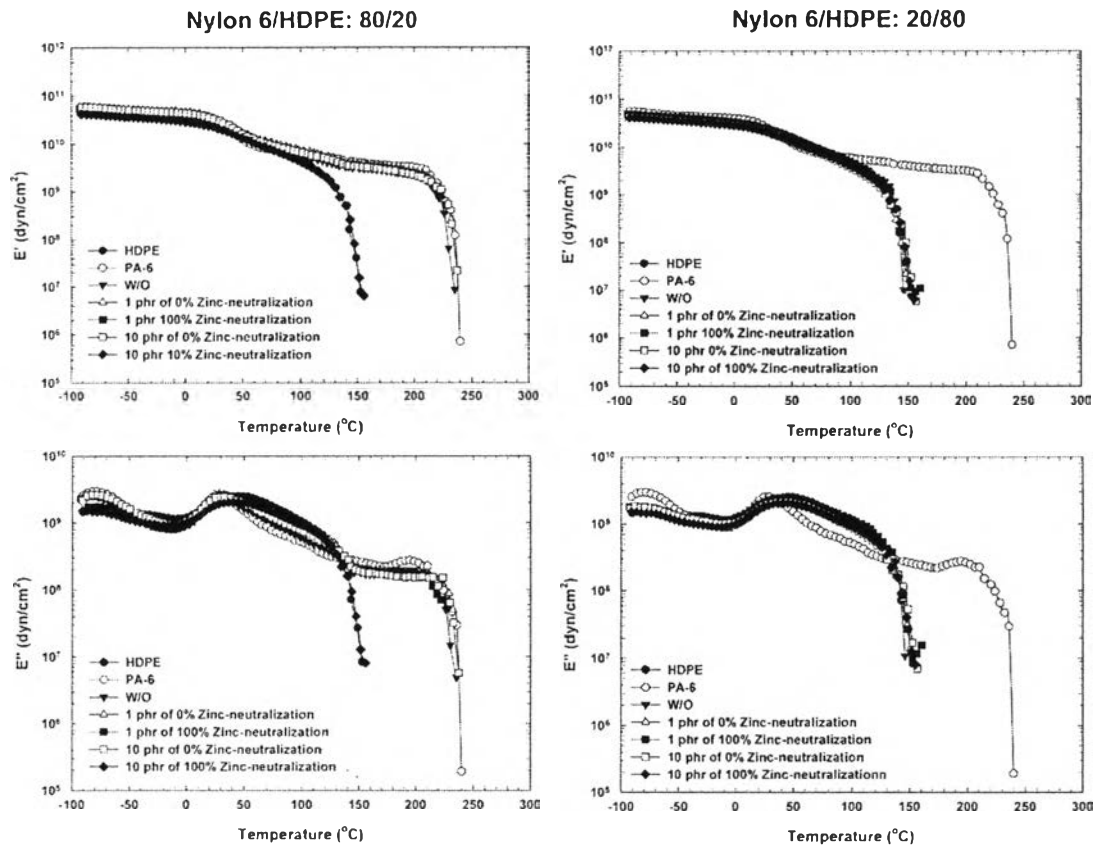


Figure 4.7 DMA spectra showing storage (E') and loss (E'') modulus for (a-b) Nylon 6 (PA-6) rich blend and (c-d) HDPE rich blend with compatibilizers.

4.4.2.5 Melt rheological properties

The apparent viscosity of neat HDPE at 240°C shown in Figure 8 was higher than that of Nylon 6 and MAH-gHDPE. The apparent shear viscosity of Nylon 6 rich blend without compatibilizer was almost the same as that of pure Nylon 6. However, the apparent shear viscosity in the Nylon 6 rich blend with MAH-gHDPE compatibilizer increased proportionally to the amount of MAH-gHDPE compatibilizer which we attribute to the formation of covalent bonds between amine or amide groups in Nylon 6 and carboxylic acids in MAH-gHDPE. Surprisingly, the melt viscosity increase at a given compatibilizer level did not depend on the neutralization level. Especially at 100% neutralization, we expected to see a smaller viscosity vs. that at lower neutralization levels due to less covalent

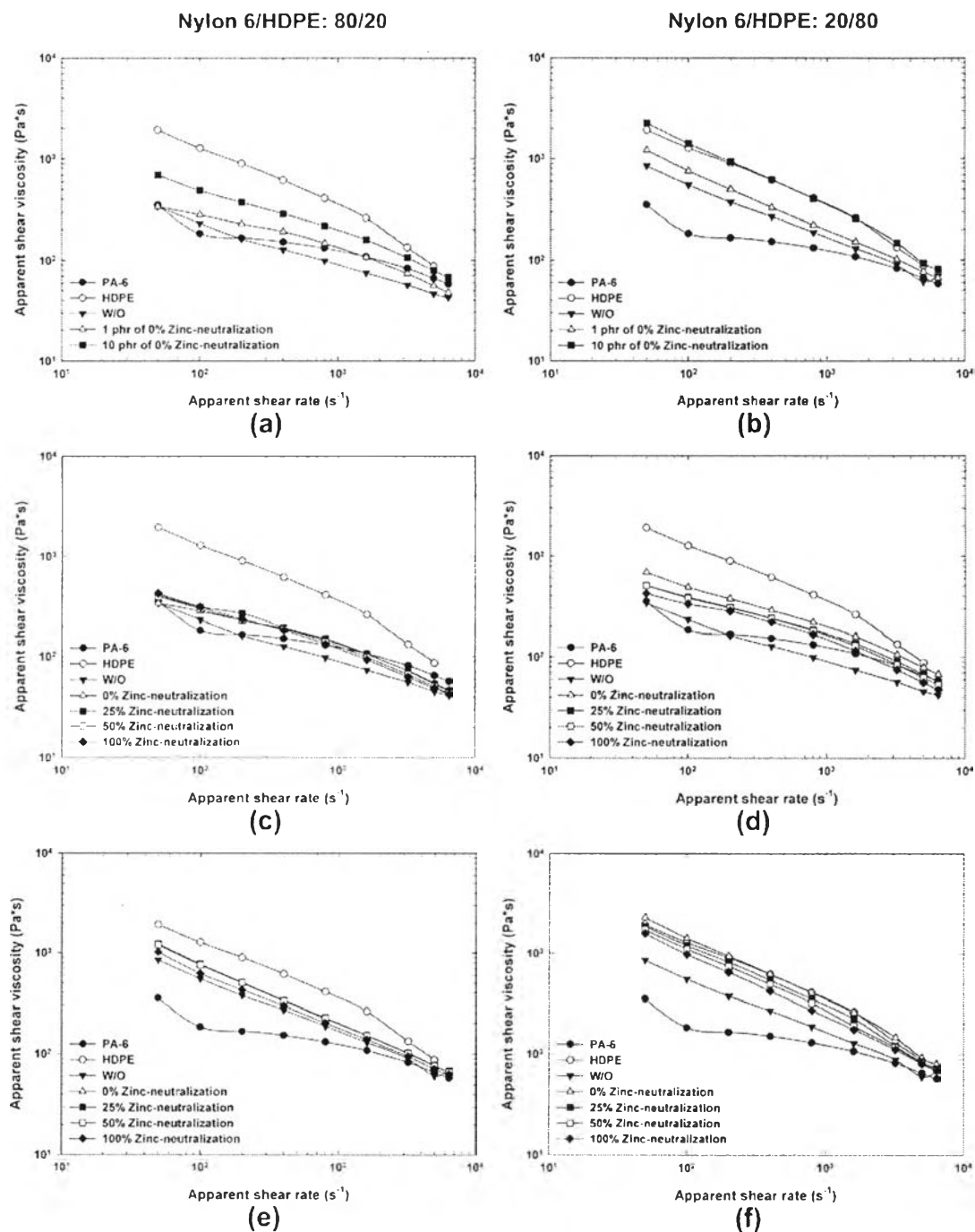


Figure 4.8 Apparent viscosity vs apparent shear rate at 240°C, (a) neat Nylon 6 (PA-6), HDPE and Nylon 6/HDPE: 80/20 (Nylon 6 rich blend) both within and without MAH-gHDPE, (b) neat HDPE and Nylon 6/HDPE: 20/80 (HDPE rich blend) both with and without MAH-gHDPE, (c) Nylon 6 rich blend with 1 phr zinc-neutralized MAH-gHDPE, (d) Nylon 6 rich blend with 10 phr zinc-neutralized MAH-gHDPE, (e) HDPE-rich blend with 1 zinc-neutralized MAH-gHDPE, and (f) Nylon 6 rich blend with 10 phr zinc-neutralized MAH-gHDPE.

bond formation as evidenced by poorer mechanical and larger dispersed phase sizes, but no change in viscosity was found.

For the HDPE rich blend, the viscosity dropped substantially with the addition of Nylon 6 to the unblended PE. An increase in viscosity with an increase in compatibilizer level was found for the HDPE rich blend as well; however, the viscosity decreased as the neutralization level increased as opposed to staying constant in the Nylon 6 rich blends. Note that this behavior is exact opposite of the viscosities of the pure compatibilizer, where an increase in neutralization leads to an increase in melt viscosity. A number of possibilities could explain this inconsistency; for example changes in miscibility of the compatibilizer with the HDPE upon neutralization, or a change in interface partitioning with neutralization.

4.5 Conclusions

Zinc-neutralized samples of maleic anhydride grafted HDPE were successfully prepared by melt neutralization with zinc acetate dihydrate using a twin-screw extruder. FTIR spectra confirmed the neutralization reaction via disappearance of maleic anhydride characteristic peaks and appearance of the zinc-carboxylate characteristic peaks. The shear viscosity increased upon neutralization as expected, although the highest viscosity was found for 75% neutralization rather than 100% neutralization. Dispersed phase sizes decreased with added compatibilizer; with 10 phr compatibilizer showing much smaller dispersed phase sizes than 1 phr compatibilizer. Compatibilization improved the mechanical properties, and the improvement at 10 phr compatibilizer for elongation at break was much more dramatic vs. 1 phr compatibilizer. A significant nucleation effect was found for the Nylon 6 upon blending. Melt viscosity results showed that increased compatibilizer level increased the melt viscosity significantly, consistent with the conclusion that covalent bonding between the Nylon 6 and the compatibilizer was occurring. The neutralization level behavior was unexpected, in the Nylon 6 rich blend the neutralization level did not affect the melt viscosity while in the HDPE rich blend, the viscosity decreased as the neutralization level increased even though pure compatibilizer showed the opposite trend. Overall, the addition of zinc did not have a

large effect on the compatibilization capabilities of the maleic anhydride grafted material; which was the same conclusion reached when zinc oxide rather than zinc acetate dihydrate was used to neutralize the compatibilizer [21].

4.6 Acknowledgements

Authors are thankful to TPE Co., Ltd., and UBE Nylon (Thailand), for providing the materials for carrying out the present work and Polymer Processing and Polymer Nanomaterials Research Unit and, Research Program in Petroleum and Petrochemical Technology (PPT consortium).

4.7 References

- [1] Z.B. Chen, T.S. Li, Y.L. Yang, Y. Zhang, S.Q. Lai. The Effect of Phase Structure on the Tribological Properties of PA66/HDPE Blends, *Macromol.Mater.Eng*, 289 (2004) 662-671.
- [2] L.A. Utracki, M.M. Dumoulin, P. Toma, Melt Rheology of High Density Polyethylen/polyamide-6 Belnds, *Polymer Engineering and Science*, 26 (1986) 34-44.
- [3] J.M. Wills, B.D. Favis, C. Lavallee, The influence of interfacial interaction an the morphology and thermal proerties of binary polymer blends., *J.Mat.Sci*, 28 (1993) 1749-1757.
- [4] J.M. Wills, B.D. Favis, Processing-morphology relationship of compatibilized polyolefin/polyamide blends. Part 1: Ther effect of an ionomer compatiblized on blend morphology, *Polymer Engineering and Science*, 28 (1988) 1416-1426.
- [5] A.R. Padwa, Compatibilized Blends of Polyamide-6 and Polyethylene, *Polymer Engineering and Science*, 32 (1992) 1703-1710.
- [6] S. Filippi, V. Chiono, G. Polacco, M. Paci, L.I. Minkova, P. Magagnini, Reactive Compatiblizer precursors for LDPE/PA6 Blends, 1 Ethylene/Acrylic acid Copolymers, *Macromol.Chem.Phys.*, 2003 (2002) 1512-1525.
- [7] M. Psarski, M. Pracella, A. Galeski, Crystal phase and crystallinity of polyamide 6/functionalized polyolefin blends, *Polymer*, 41 (2000) 4923-4932.
- [8] W. Qiu, K. Mai, K. Fang, Z. Li, H. Zeng, Morphology and Thermal Behavior of PA1010/LLDPE Blends using PE-g-AA as a compatibilizer, *Journal Applied Polymer Science*, 71 (1999) 847-853.
- [9] K. Chandramouli, S.A. Jabarin, Morphology and Property Relationships in Ternart Blends of Polyethylene/Polyamide-6/Compatibilizing Agents, *Advances in Polymer Technology*, 14 (1995) 35-46.
- [10] R. Guruprasad, M. Chanda, Solution Grafting of Maleic Anhhydride onot Polyethylene and Compatibilization of Polyethylene-Nylon Blends, *J.Polym.Mater*, 16 (1999) 173-178.

- [11] F. Ide, A. Hasegawa, Studied on Polymer Blends of Nylon 6 and Polypropylene or Nylon 6 and polystyrene Using the Reaction of polymer, *Journal Applied Polymer Science*, 18 (1974) 963-974.
- [12] C. Jiang, S. Filippi, P. Magagnini, Reactive compatibilizer precursors for LDPE/PA6 blends. II: maleic anhydride grafted polyethylenes, *Polymer*, (2003) 2411-2422.
- [13] B.K. Kim, S.Y. Park, S.J. Park, Morphological, Thermal and Rheological Properties of Blends: Polyethylene/Nylon-6, polyethylene/nylon-6/(Maleic anhydride-g-Polyethylene) and (Maleic anhydride-g-Polyethylene)/Nylon-6, *Eur.Polym.J.*, 27 (2009) 349-354.
- [14] C.H. Qiu, V. Komppa, A. Sivola, Compatibilized Polyamide/Ultra High Molecular Weight polyethylene Blends, *Polymer & Polymer Composites*, 5 (1997) 423-430.
- [15] Z. Yao, Z. Yin, G. Sun, C. Liu, J. Tong, L. Ren, J. Yin, Morphology, Thermal Behavior, and mechanical properties of PA6/UHMWPE Blends with HDPE-g-MAH as a Compatibilizing Agent, *J Appl Polym Sci*, 75 (2000) 232-238.
- [16] R.A. Kudva, H. Keskkula, D.R. Paul, Morphology and mechanical properties of compatibilized nylon 6/polyethylene blends, *Polymer*, 40 (1999) 6004-6021.
- [17] L. Pan, T. Chiba, T. Inoue, Reactive blending of polyamide with polyethylene: pull-out of in situ-formed grafted copolymer, *Polymer*, 42 (2001) 8825-8831.
- [18] P. Leewajanukul, R. Pattanaolarn, J.W. Ellis, M. Nithitanukul. B.P. Grady, Use of zinc-neutralized ethylene/methacrylic acid copolymer ionomers as blend compatibilizers for nylon 6 and low-density polyethylene, *J. Appl. Polym. Sci.*, 89 (2003) 620-629.
- [19] A. Lahor, M. Nithitanukul, B.P. Grady, Blends of low-density polyethylene with nylon compatibilized with a sodium-neutralized carboxylate ionomer, *Eur Polym J*, 40 (2004) 2409-2420.
- [20] W. Sinthavathavorn, M. Nithitanukul, R. Magaraphan, B.P. Grady, Blends of polyamide 6 with low-density polyethylene compatibilized with ethylene-methacrylic acid based copolymer ionomers: Effect of neutralizing cations, *J. Appl. Polym. Sci.*, 107 (2008) 3090-3098.

- [21] B. Chatreenuwat, M. Nithitanakul, B.P. Grady, The effect of zinc oxide addition on the compatibilization efficiency of maleic anhydride grafted high-density polyethylene compatibilizer for high-density polyethylene/polyamide 6 blends, *J. Appl. Polym. Sci.*, 103 (2007) 3871-3881.
- [22] W. Sinthavathavorn, M. Nithitanakul, B.P. Grady, R. Magaraphan, Melt rheology of low-density polyethylene/polyamide 6 using ionomer as a compatibilizer, *Polymer Bulletin*, 61 (2008) 331-340.
- [23] W. Sinthavathavorn, M. Nithitanakul, B.P. Grady, R. Magaraphan, Melt rheology and die swell of PA6/LDPE blends by using lithium ionomer as a compatibilizer, *Polymer Bulletin*, 63 (2009) 23-35.
- [24] P. Antony, S. Bandyopadhyay, S.K. De, Thermoplastic elastomers based on ionomeric polyblends of zinc of maleated polypropylene and maleated EPDM Rubber, *Polymer Engineering and Science*, 39 (1999) 963-974.
- [25] H. Gunzler, H.-U. Gremlich, *IR Spectroscopy*; WILEY-VCH Verlag GmbH, Weinheim, 2002.
- [26] T. Ishioka, Infrared spectral change in a zinc salt of an ethylene-methacrylic acid ionomer on water absorption, *Polymer Journal*, 25 (1993) 1147-1152.
- [27] B.P. Grady, J.G.P. Goossens, M.E.L. Wouters, Morphology of Zinc-Neutralized Maleated Ethylene-Propylene Copolymer Ionomers: Structure of Ionic Aggregates As Studied by X-ray Absorption Spectroscopy, *Macromolecules*, 37 (2004) 8585-8591.