

Properties of Bloodmeal/Linear Low-Density Polyethylene Blends Compatibilized with Maleic Anhydride Grafted Polyethylene

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ABSTRACT: Novatein thermoplastics from bloodmeal (NTP) were blended with linear low-density polyethylene (LLDPE) using maleic anhydride grafted polyethylene (PE-g-MAH) as compatibilizer. The compatibilizing effect on mechanical, morphology, thermal properties, and water absorption were studied and compared with blends without compatibilizer. The amount of polyethylene added was varied between 20 and 70% in NTP with addition of 10% compatibilizer. An improvement in compatibility between NTP and LLDPE was observed across the entire composition range and the difference were more pronounced at higher NTP contents where the tensile strength of blends was maintained and never dropped below that of pure NTP. Theoretical models were compared to the results to describe mechanical properties. A finely dispersed small particles of NTP in compatibilized blends were observed using SEM. Improved compatibility has restricted chain movement resulting in slightly elevated T_g revealed by DMA. On the other hand, water absorption of the hydrophilic NTP has been decreased when blending with hydrophobic LLDPE. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 130: 1890–1897, 2013

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INTRODUCTION

Meat is New Zealand's second-largest food export and is worth \$5.14 billion.¹ One of the by-products from meat processing is bloodmeal, an insoluble powder of dried blood containing at least 86 wt % protein and <10% moisture. It is one of the highest non-synthetic sources of nitrogen coming from meat processing. Natural proteins are linear, unbranched and have a precise length with a molecular diversity consisting of up to different 20 amino acids as monomers. An understanding of the chemical reactivity of the amino acid functional groups is important because they provide many reaction sites for potential crosslinking or chemical grafting. Beef blood meal contains more lysine, threonine, valine, leucine, tyrosine, and phenylalanine while pork blood meal contains more histidine, arginine, proline, glycine, and isoleucine.² Of these, cysteine and lysine are the most reactive amino acids.

Utilization of bloodmeal as a bioplastic is an alternative to synthetic polymers and may offer a sustainable option over raw materials competing with food sources. It has been shown that bloodmeal can be converted into a Novatein thermoplastic (NTP) by using an appropriate combination of additives, followed by extrusion.^{3–5} However, the material is very brittle and water sensitive which may limit its potential applications.

In general, developing blended materials with a full set of desired properties is much more effective and cheaper compared to synthesizing new polymers.^{6,7} Linear low-density polyethylene (LLDPE) is among the most popular polyethylene products with significant numbers of short branches, commonly made by copolymerization of ethylene with longer-chain olefins. LLDPE is not biodegradable, however some believe that by blending it with biodegradable thermoplastics, the inert components will slowly decompose and disappear as long as the particle size of the thermoplastic resin is fine enough.^{8,9} Blending LLDPE with natural polymers such as soy protein,^{10–12} and starch^{13–22} has become an important research interest in degradable plastics. However, most blends involving natural and synthetic polymer are immiscible due to the absence of specific interactions, thus requiring a compatibilizer to achieve miscibility.

Maleic anhydride is one of the popular choices used as monomer to graft onto polypropylene, polyethylene, and various other polymers.^{23–25} PE-g-MAH has hydrophilic and hydrophobic end tail that can react with protein or starch and compatibilize of PE and polyolefin. The mechanical properties of LDPE and starch were reduced by increasing starch content despite the fact that the dispersion of starch particles improved after the addition of PE-g-MAH.^{21,26} Research found that improved compatibility between rice starch and LDPE from PE-g-MAH was

attributed to the chemical reaction between hydroxyl groups in starch and anhydride groups in PE-g-MAH as well as the physical interaction between PE chains in PE-g-MAH and bulk LDPE.¹³ A finely dispersed morphology of starch particles of about 5–10 μm was observed between LLDPE and thermoplastic starch, indicating good interfacial adhesion.¹⁵ Anhydride groups were also found effective to improve the compatibility between immiscible blends of soy protein and thermoplastic polyesters.²⁷ It was found that the glass transition temperature and thermal properties of the protein and polymer remained unchanged even after blending. In a different study, reactive compatibilizers for starch–polycaprolactone (PCL) blends were synthesized and was found that PCL-g-diethyl maleate (PCL-g-DEM) was a more efficient compatibilizer than PCL-g-glycidyl methacrylate (PCL-g-GMA).²⁸

Modeling Mechanical Properties

The behavior of polymer blends in this work was modeled using known relationships that have been used to predict properties of polymer blends and composites. These models were developed for spherical particles distributed in the matrix. For NTP, it is assumed as near-spherical particles therefore Kerner and Hashin equation was used. Kerner and Hashin considered the dispersed polymer phase as spheroidal in shape and modeled the blend's modulus using equation:²⁹

$$E = E_1 \frac{\frac{\phi_2 E_2}{(7-5\nu_1)E_1 + (8-10\nu_1)E_2} + \frac{\phi_1}{15(1-\nu_1)}}{\frac{\phi_2 E_1}{(7-5\nu_1)E_1 + (8-10\nu_1)E_2} + \frac{\phi_1}{15(1-\nu_1)}} \quad (1)$$

where E , E_1 , and E_2 are the modulus for the binary blend, the matrix and the dispersed phase respectively; ϕ_1 and ϕ_2 are the volume fractions of the matrix and the dispersed phase, respectively; ν_1 is the Poisson's ratio for the matrix.

In eq. (1), perfect adhesion is assumed between the two polymer phases; however, this is often not the case. In the absence of adhesion, the Kerner equation is simplified by assuming E_2 to be zero

$$E = E_1 \frac{(7-5\nu_1)\phi_1}{15(1-\nu_1)\phi_2 + (7-5\nu_1)\phi_1} \quad (2)$$

The elongation at break for polymer and composites can be evaluated using Nielsen model. Typically, a decrease in elongation at break is observed with increase in filler content, and assuming a spherical dispersed polymer phase, the Nielsen model can be used.³⁰ For good adhesion between phases, the following Nielsen equation is approximately correct:

$$\varepsilon_c = \varepsilon_0 \left(1 - \phi^{1/3}\right) \quad (3)$$

where ε_c is the elongation at break of the blends and ε_0 is the elongation at break of polymer constituting the matrix. The tensile strength is expected to decrease with an increase of dispersed particle (or dispersed polymer phase) content. The theoretical values of tensile strength have been modeled by Nicolais and Narkis³¹ assuming no adhesion between phases and

failure is at the filler–matrix interface. In eq. (4), σ_c is the composite's tensile strength and σ_m is the polymer matrix's tensile strength:

$$\sigma_c = \sigma_m \left(1 - 1.21\phi^{2/3}\right) \quad (4)$$

In this study, NTP was blended with low linear density polyethylene (LLDPE) in different proportions containing PE-g-MAH as compatibilizer. The effect of PE-g-MAH on the materials water absorption and mechanical properties were analyzed in light of the resultant blend's morphology. Modeling of mechanical properties were also performed and correlated to observed values.

MATERIALS AND METHODOLOGY

Materials

Bloodmeal was supplied by Wallace Corporation (New Zealand) and sieved to an average particle size of 700 μm and is mostly bovine with some chicken blood. Technical grade sodium dodecyl sulfate (SDS) and analytical grade sodium sulfite were purchased from Biolab Nz and BDH Lab Supplies. Agricultural grade urea was obtained from Balance Agri-nutrients (NZ). LLDPE, Cotene 3901 was purchased from J.R. Courtenay (N.Z.). Polyethylene-*graft*-maleic anhydride (PE-g-MAH) and triethyl was purchased from Sigma Aldrich (NZ). Triethylene glycol was purchased from Merck (NZ).

Preparation of Novatein Thermoplastic Protein (NTP)

Samples were prepared by dissolving urea (20 g), sodium dodecyl sulfate (6 g) and sodium sulfate (6 g) in water (80g). The solution was heated until the temperature reached 50–60°C followed by blending with bloodmeal powder (200 g) in a high-speed mixture for 5 min. Triethylene glycol (40 g) was added to the mixture and blended for another 3–4 min. The mixtures were stored for at least 24 h prior to extrusion. NTP, LLDPE and PE-g-MAH were mixed in a plastic zip-lock bag prior to extrusion.

Extrusion

Extrusion was performed using a Thermo Prism TSE-16-TC twin screw extruder at a screw speed of 150 rpm and temperature settings of 70, 100, 100, 100, 120°C from feed to exit die. The screw diameter was 16 mm at L/D ratio of 25 and was fitted with a single 10-mm circular die. A relative torque of 50–60% was maintained, by adjusting the mass flow rate of the feed. The extrudate was granulated using a triblade granulator from Castin Machinery, New Zealand.

Injection Molding

Standard tensile bars (ASTM D638) were prepared using a BOY 35A injection molder with a temperature profile of 100, 115, 130, 135, and 140°C from feed to exit die.

Mechanical Testing

Tensile specimens were tested on an Instron model 4204 according to ASTM D638-86. For each experiment five specimens were conditioned at 23°C and 50% relative humidity, equilibrating to ~10% moisture content and tested at a crosshead speed of 1 mm min⁻¹ using 5-kN load cell. Tensile strength,

Table I. Formulations of NTP/LLDPE Blends and Control Samples

Sample name	NTP (wt %)	LLDPE (wt %)	PE-g-MAH (wt %)
0 NTP	0	100	0
20 NTP	20	70	10
30 NTP	30	60	10
40 NTP	40	50	10
50 NTP	50	40	10
60 NTP	60	30	10
70 NTP	70	20	10
100 NTP	100	0	0

elongation at break and Young's modulus were analyzed for conditioned samples.

Morphology

The microstructure of NTP/LLDPE was assessed using a field emission scanning electron microscope (SEM) Hitachi S-4700. Samples were immersed in liquid nitrogen and the fracture surfaces were sputter-coated with platinum before scanning. An accelerating voltage of 5 kV was applied.

Water Absorption

All samples were oven dried at 80°C until constant weight. Dried samples were immersed in water at room temperature for total of 9 days. Samples were removed from water, blotted with tissue paper to remove excess water and then weighed. The water absorption was calculated on a dry sample weight basis.

Simultaneous DSC-TGA (SDT)

Thermogravimetric analysis of pure LLDPE and blended samples were measured using a TA instrument SDT 2960. The samples were sealed in aluminum pan and tested from 50 to 800°C at a heating rate 10°C min⁻¹ using air.

Dynamic Mechanical Analysis (DMA)

Dynamic mechanical properties of NTP/LLDPE were studied using a Perkin Elmer DMA 8000 fitted with a high temperature furnace and controlled with DMA software version 14306. DMA specimens (30 × 6.5 × 3 mm³) were cut from injection molded samples and tested using a single cantilever fixture at 1-Hz vibration frequency in temperature range of -80–120°C.

Formulations

Table I lists the formulations of all samples studied in this work. NTP was extruded and injection molded with LLDPE using the same profile as above. NTP was produced first, followed by blending with the required LLDPE and compatibilizer after which it was extruded again.

RESULTS AND DISCUSSION

Mechanical Properties

Figure 1(a) shows the tensile strength of NTP/LLDPE blends with and without compatibilizer. LLDPE had a tensile strength of 14 MPa while that of NTP is only 6.2 MPa. It would therefore be expected that the blend's tensile strength would be some intermediate value of these. However, the specific value would

depend on the phase morphology as well as adhesion between phases.

The tensile strength of blends without compatibilizer decreased with increasing NTP contents. Above 50 wt % it dropped to values less than pure NTP, most likely due to lack of compatibility between NTP and LLDPE. This observation is in agreement with the fact that blending synthetic and natural polymers are challenging because of their dissimilar nature. NTP is hydrophilic while LLDPE is hydrophobic and the difference resulted in separation of two phases. In polymer blends it is often observed that either one of the two polymers will be the dispersed phase or the other is a continuous phase. Which polymer forms the specific phase is dependent on the amount

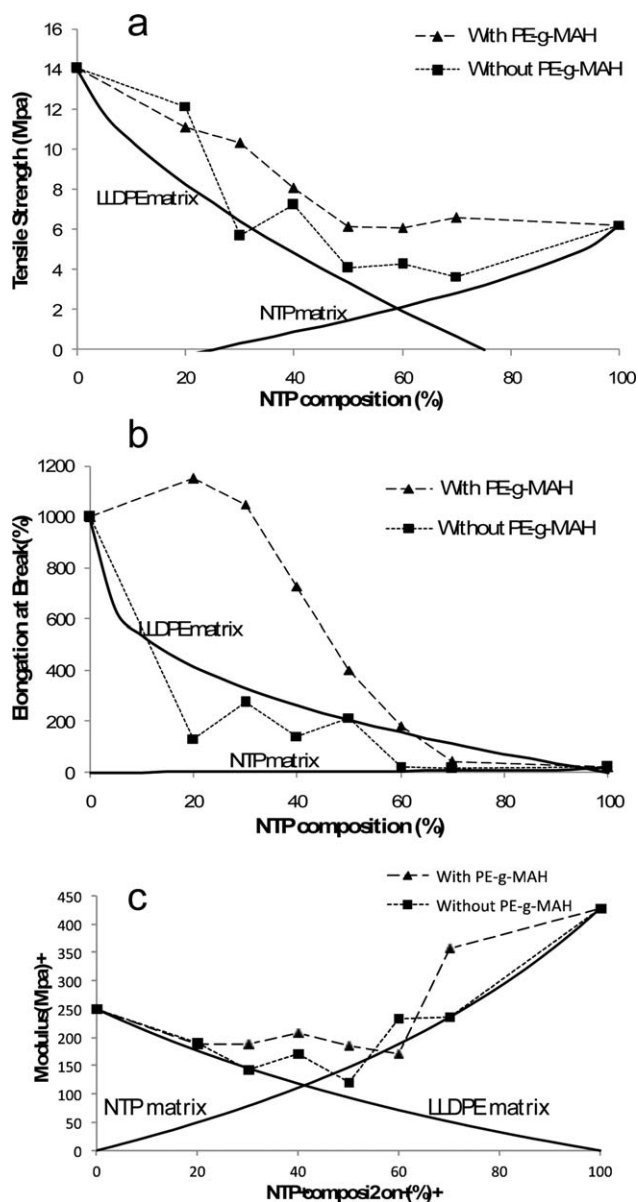


Figure 1. Mechanical properties of NTP/LLDPE blend with and without PE-g-MAH. (a) Tensile strength, (b) Elongation at break, and (c) Young's modulus. Relevant models also included using either NTP or LLDPE as matrix.

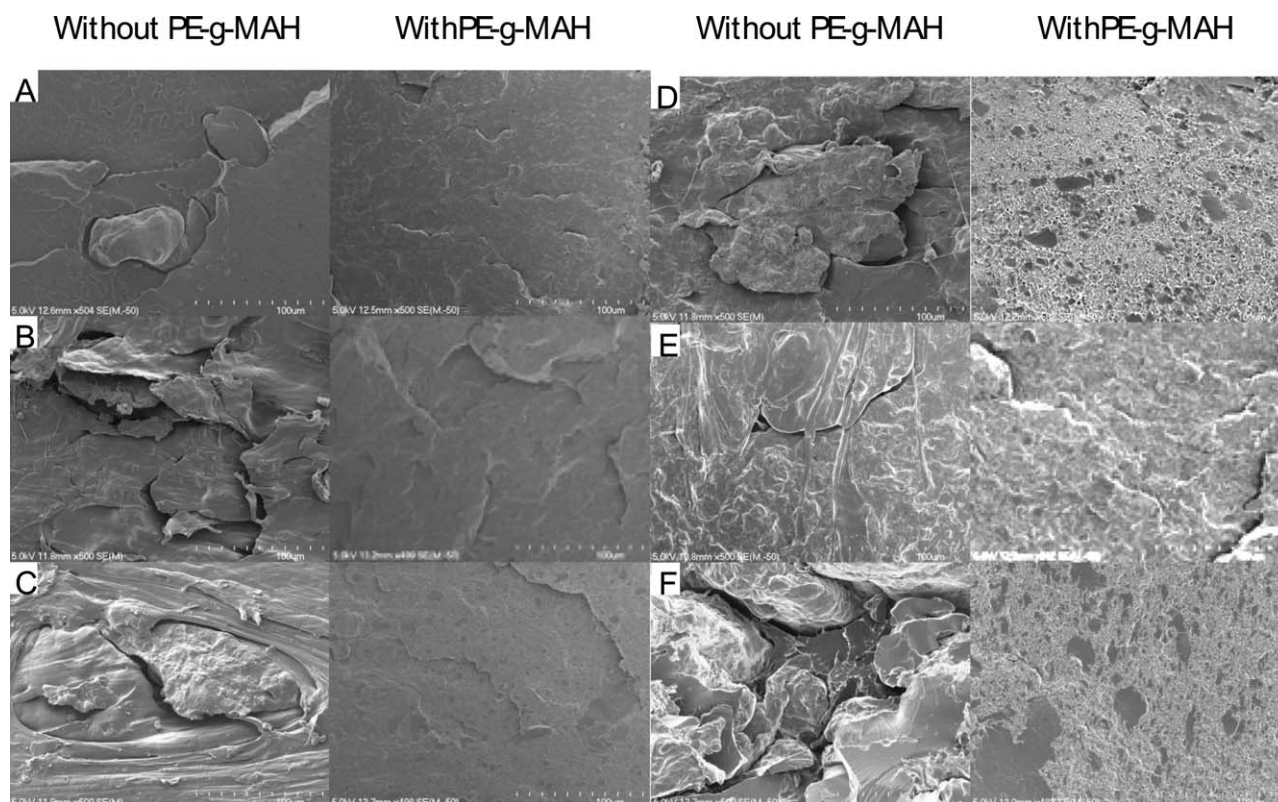


Figure 2. SEM morphology of NTP/LLDPE blends without PE-g-MAH and with PE-g-MAH (a: 20 NTP, b: 30 NTP, c: 40 NTP, d: 50 NTP, e: 60 NTP, f: 70 NTP).

present. Results would suggest that NTP formed a dispersed phase at low NTP content and LLDPE forming the dispersed phase a high NTP content, with significant lack of phase compatibility leading to the low tensile strength of the blends.

A similar decrease in tensile strength was observed for blends containing PE-g-MAH, however, the tensile strength leveled off at about 50 wt % NTP, never dropping below that of pure NTP. It was thought that increased interfacial adhesion lead to this behavior leading to blends with increased tensile strength over those without PE-g-MAH. As concentration increased, some phase inversion may have occurred leading to a region where neither polymer was the dispersed phase. It was thought that at almost equal proportions, a cocontinuous phases-morphology could have lead to the observed increase in strength and was further explored using SEM.

Elongation at break for blends without PE-g-MAH showed a very sharp drop at low NTP content. Considering that NTP is much more brittle than LLDPE (20% vs. 1100%), the result is not surprising and is similar to what is expected of particulate composites with poor interfacial adhesion or the addition of second immiscible phase to a ductile material.³² Relevant models also included using either NTP or LLDPE as matrix.

In the case of compatibilized blends the situation was completely different. After an initial increase, the elongation at break dropped gradually from that of LLDPE. The synergistic effect at 20–30% of NTP was consistent with findings by Walia et al.³³ using PHEE and starch with different moisture contents.

Despite the decrease over that of pure LLDPE, elongation was always higher to blends without a compatibilizer. It was concluded that the phase morphology must be the determining factor governing changes in the observed mechanical properties. At low NTP content, sufficient interfacial adhesion leads to high elongation to break values, despite the inclusion of a more brittle NTP phase. As the proportion NTP increased, the elongation did decrease as the blend's behavior approached that of pure NTP. Based on the tensile strength at high NTP content, it was concluded that NTP must form a continuous phase under these conditions. This would be consistent to previous observation, which suggested that as the volume fraction of minor

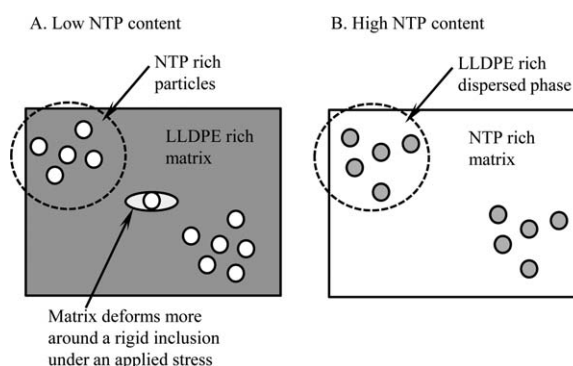


Figure 3. Schematic illustration of NTP/LLDPE blends when LLDPE as the matrix (a) and NTP as the matrix (b).

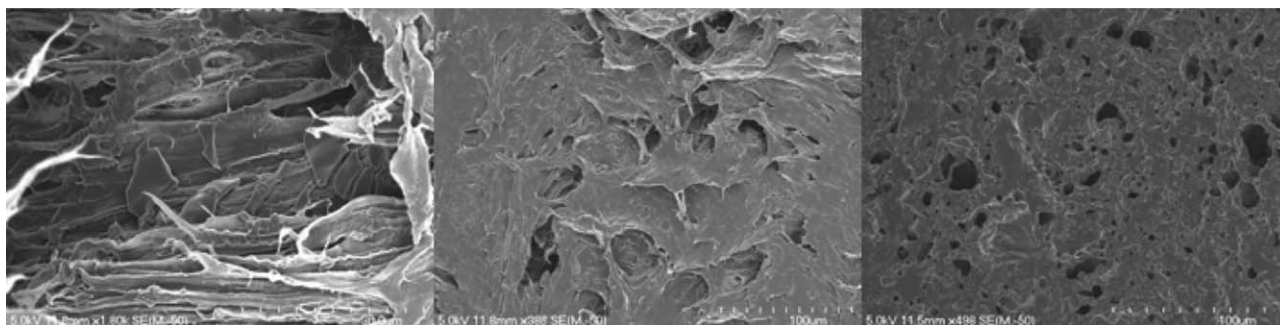


Figure 4. SEM of compatibilized blends containing 50, 60, and 70 wt % NTP after digestion in nitric acid.

components increases, the morphology would change from a dispersed phase to the continuous phase.³⁴

The Young's modulus for blends with and without PE-g-MAH showed very similar trends. A sharp drop in modulus was observed with the inclusion of NTP, but increased with increasing NTP content above 50 wt % NTP in the absence of PE-g-MAH or 70 wt % with PE-g-MAH. NTP has a higher modulus than LLDPE and the results would be consistent to what is expected of including rigid particles in a ductile matrix. At low filler content, the disruption of chain interaction could lead to a reduction in modulus, but when as filler content is increased chain mobility is restricted leading to an increase in modulus. However, tensile strength and elongation at break values suggested that NTP formed the continuous phase at high NTP content. All the blends tested had a modulus lower of either of the polymers, suggesting that either dispersed phase disrupted chain interaction, as explained earlier.

In this study, theoretical models were used as interpretation of the mechanical property results. The Poisson's ratio for NTP was assumed to be 0.3 and for LLDPE is 0.5. To estimate the volume fractions, a density of 1.2 and 0.9 g cm⁻³ were used for NTP and LLDPE, respectively.

In the Kerner model, poor interfacial adhesion is assumed and most successfully described Young's Modulus using NTP as matrix in the absence of PE-g-MAH. The assumption of LLDPE being the dispersed phase would appear to be reasonable in light of these results.

The theoretical values of tensile strength have been calculated using the Nicolais–Narkis model, which assumes no adhesion between NTP and LLDPE. Experimental values with and without compatibilizer was significantly higher than theoretical values, but compatibilized blends suggested that there is strong adhesion between NTP and LLDPE when PE-g-MAH was added. This result is in agreement with the starch-LDPE with PE-g-MA blends properties that have been reported by others.^{13,26,35}

Elongation at break calculated from the Nielsen model is plotted in Figure 1(b). The most obvious indication of good adhesion between NTP and LLDPE when PE-g-MAH was added to the blends were seen from elongation at break values. The Nielsen model did not show agreement with experimental values,

except at high NTP content for blends without PE-g-MAH. For compatibilized blends, the model underestimated the behavior, but at about 50 wt % NTP the Nielsen model was unable to predict elongation at break, using either polymer as matrix.

Morphology

Fracture surfaces of blends with and without PE-g-MAH are shown in Figure 2. Samples without compatibilizer showed two distinct phases at all compositions. It was clear that at low NTP content, NTP formed the dispersed phase with relatively large particles. The incompatibility between the two polymers was suspected to lead to large domains of NTP-rich particles suspended in a weak matrix of mostly LLDPE. This result was supported by mechanical properties where at NTP content between 20 and 30% the tensile strength dropped rapidly indicating that the dispersion of NTP has disrupted the LLDPE matrix. Veenstra et al.³⁶ suggested that when a stiff component (NTP-rich phase) is the minor phase, the weak matrix (LLDPE rich) will deform most at the interface between the stiff droplets and the weak matrix, as illustrated in Figure 3(a). The elongation properties obtained at low NTP is mainly contributed by LLDPE polymer matrix and quickly diminishes with increasing NTP content.

In the case of NTP contents >50%, the influence of a dispersed phase (LLDPE rich) will be limited as the continuous phase will contain mostly NTP, further decreasing the elongation at break.

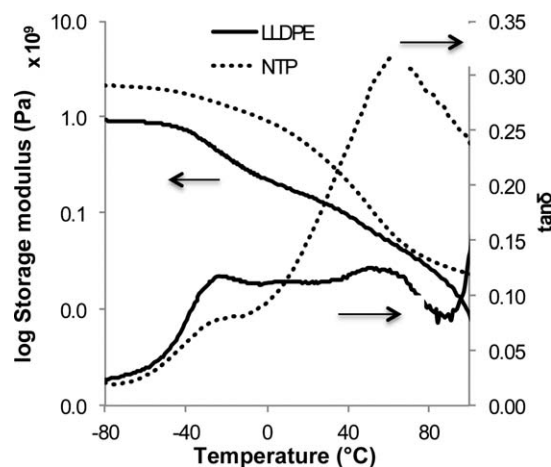


Figure 5. DMA thermograms of LLDPE and NTP.

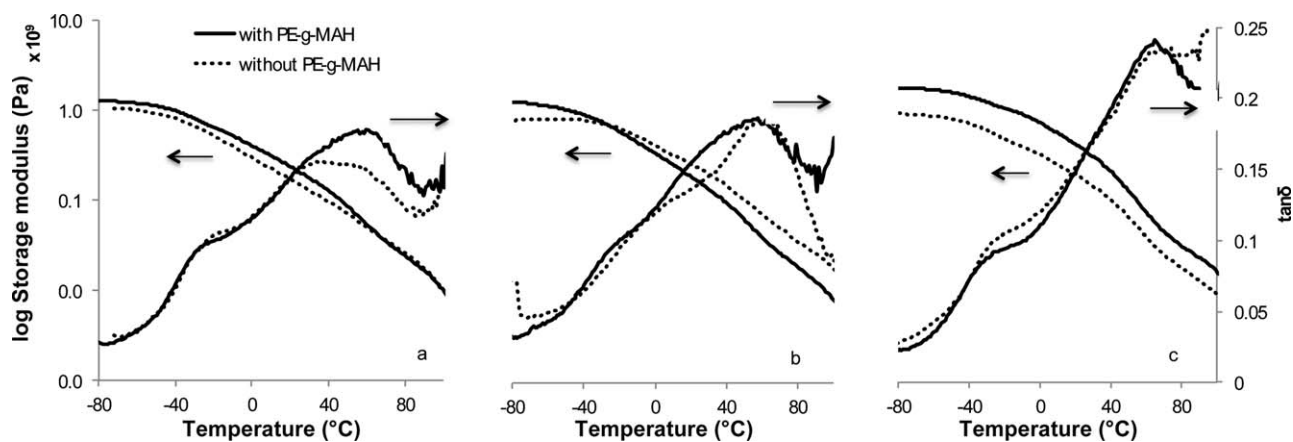


Figure 6. DMA thermograms of blends of (a) 40 wt % NTP, (b) 50 wt % NTP, and (c) 60 wt % NTP with and without compatibilizer.

In all cases where a dispersed phase was observed, a very rough fracture surface was evident with a clear separation between the phases. Poor interfacial adhesion would therefore account for the observed low strength and elongation at break.

During dispersive mixing, the size of minor cohesive component is reduced while distributive mixing is the process of dispersing the minor component throughout the matrix.³⁷ Including PE-g-MAH as compatibilizer, a large improvement in dispersion was observed. It was difficult to distinguish between different phases and the fracture surfaces appeared smooth suggesting fine dispersion between the phases.³⁸ Some interfacial boundaries were observed as ridges, as indicated in Figure 2(a). At 40% NTP, a second finely dispersed phase appeared and was thought to be an NTP-rich phase. There was no clear separation between these phases, suggesting good interfacial adhesion. This was supported by earlier observations regarding improved mechanical properties. It is known that at the point of phase inversion, cocontinuous morphologies are mainly formed. Above 50% NTP a clear LLDPE rich phase was evident from ductile fracture regions. NTP appeared to have formed a co-continuous phase with LLDPE, but in addition, larger NTP rich particles were also observed at higher NTP levels (70%).

The interesting phase morphology in the compatibilized blends above 50 wt % NTP was further explored by digesting the protein phase using nitric acid. LLDPE is not digested using this acid, which would reveal the morphology of the LLDPE phase in the blends. In Figure 4, SEM images of compatibilized blends after digestion are shown. Considering NTP was the major constituent, only a small amount of material has been removed after digestion. This would suggest the presence of a finely dispersed NTP phase as well as a LLDPE-rich phase which prevented NTP removal during digestion. This would be consistent to the observed ductile fracture regions observed in the compatibilized blends (Figure 2).

It was concluded that 10% PE-g-MAH was sufficient to compatibilize NTP and LLDPE. The addition of compatibilizer has reduced the interfacial tension between the phases, increased the surface area of the dispersed phase, improves adhesion and

stabilized the phase morphology, consistent with other research.¹⁵ The mechanism of compatibilizing was thought to be through ester bond formation of anhydride groups in PE-g-MAH and amine groups on protein chains, and chain entanglement between PE-g-MAH and LLDPE.

DMA Analysis

The DMA thermograms for NTP and LLDPE are shown in Figure 5. NTP had a glass transition (T_g) at $\sim 60^\circ\text{C}$ as well as a β -transition at about -20°C , consistent with earlier findings.³⁹ LLDPE had a T_g at about -20°C as well as a transition associated with amorphous regions trapped within crystalline regions at just under 60°C .^{40,41}

Thermograms for blends containing 40, 50, and 60 wt % NTP are shown in Figure 6. It can be seen that all samples exhibited two glass transition temperatures between that of NTP and LLDPE. Including PE-g-MAH raised the T_g associated with the NTP rich phase and the storage modulus was also slightly higher in these blends. It was thought that the addition of PE-g-MAH improved compatibility, thereby restricting chain

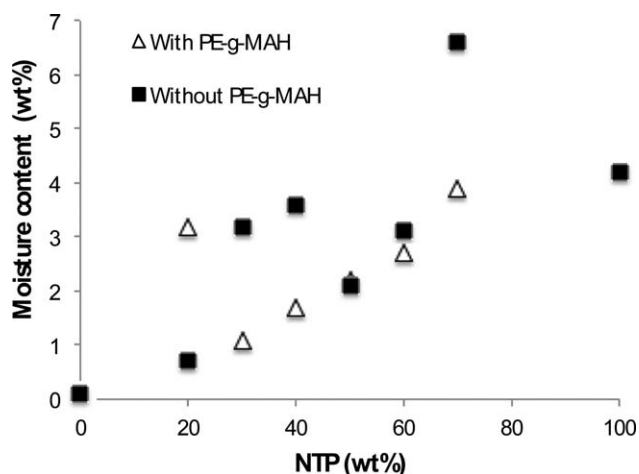


Figure 7. Equilibrium moisture content determined as mass loss percentage at 120°C .

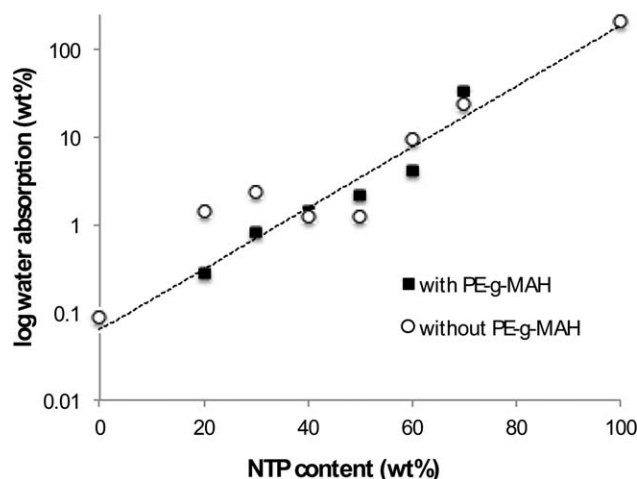


Figure 8. Effect of PE-g-MAH on water absorption (%) of NTP/LLDPE blends after 24 h.

movement resulting in a slightly higher T_g , but only when the NTP fraction was low.

Water Absorption

One of the largest challenges with protein-based plastics are their water sensitivity, attributed to their hydrophilic nature. Blending with a hydrophobic polymer, such as LLDPE, could greatly improve water resistance. From Figure 7, it can be seen that the equilibrium moisture content increased with increasing NTP content. In most cases, compatibilization further reduced the moisture content. Moisture content was taken as the percentage mass loss at 120°C using thermogravimetric analysis.

Samples were also immersed in water for a period of 9 days. Absorption occurred rapidly within a day regardless the amount of LLDPE added. Figure 8 shows the results for water absorption after a period of 1 day. NTP absorbed the most (214 wt %) as a consequence of hydrophilic nature, compared to hydrophobic LLDPE, which absorbed only 0.09 wt %. Blending these two polymers was expected to decrease the water absorption of NTP. From Figure 8, it can be seen that water absorption decreased with decreasing NTP.

Including PE-g-MAH lead to a slight decrease in water absorption, probably because PE-g-MAH improved dispersion of NTP in the LLDPE matrix at low NTP content. Virtually no difference between blends with or without compatibilizer was observed at high NTP content.

CONCLUSION

NTP/LLDPE blends with addition of 10% of PE-g-MAH were shown to be more compatible as evident from a more homogeneous distribution of the dispersed phase as well as a finer dispersion of each phase. The morphology of compatibilized blends suggested a cocontinuous phase at NTP >50 wt %. It was concluded that a 50 wt % NTP without PE-g-MAH, a phase inversion must have occurred as evident from a significant increase in tensile properties. Using PE-g-MAH also prevented the blends mechanical properties to be less than that of pure NTP, at any level of LLDPE. PE-g-MAH could be

considered as a suitable candidate to toughen NTP/LLDPE blends as evident from the change to more ductile fracture surfaces of blended samples. LLDPE has significantly reduced the water absorption of NTP, but improved phase morphology did not further improve this at high NTP content.

REFERENCES

1. New Zealand Trade and Enterprise, Available at: http://cache.business.newzealand.com/vAmseKA/media/103386/meat_industry_fact_sheet.pdf (accessed August 3, 2011).
2. Kramer, S. L.; Waibel, P. E.; Behrends, B. R.; El Kandelgy, S. M. *J. Agric. Food Chem.* **1978**, *26*, 979.
3. Verbeek, C. J. R.; van den Berg, L. E. *J. Polym. Environ.* **2010**, *19*, 1.
4. Verbeek, C. J. R.; van den Berg, L. E. *Macromol. Mater. Eng.* **2010**, *295*, 10.
5. Verbeek, C. J. R.; van den Berg, L. E. *Macromol. Mater. Eng.* **2011**, *296*, 524.
6. Paul, D. R.; Newman, S. *Polymer Blends*; Academic Press: New York, **1978**.
7. Rudin, A. *J. Macromol. Sci. C Polym. Rev.* **1980**, *19*, 267.
8. Janssen, L. Leszek Mościcki, *Thermoplastic Starch: A Green Material for Various Industries*; Wiley-VCH Verlag GmbH & Co. KGaA, **2010**, p 119–148.
9. Utracki, L. A. *Commercial Polymer Blends*; Chapman & Hall, London SE1 8HN, UK, **1998**.
10. Kaur, I.; Bhalla, T. C.; Deepika, N.; Gautam, N. *J. Appl. Polym. Sci.* **2009**, *111*, 2460.
11. Sam, S. T.; Ismail, H.; Ahmad, Z. *J. Vinyl Addit. Technol.* **2009**, *15*, 252.
12. Ting, S. S.; Ismail, H.; Ahmad, Z. *J. Vinyl Addit. Technol.* **2012**, *18*, 57.
13. Wang, Y. J.; Liu, W.; Sun, Z. *J. Appl. Polym. Sci.* **2004**, *92*, 344.
14. Liu, H.; Wu, Q.; Zhang, Q. *Bioresour. Technol.* **2009**, *100*, 6088.
15. Wang, S.; Yu, J.; Yu, J. *J. Appl. Polym. Sci.* **2004**, *93*, 686.
16. Vieyra Ruiz, H.; Martínez, E. S. M.; Méndez, M. Á. A. *Starch—Stärke* **2010**, *63*, 42.
17. Vaidya, U. R.; Bhattacharya, M.; Zhang, D. *Polymer* **1995**, *36*, 1179.
18. Vaidya, U. R.; Bhattacharya, M. *J. Appl. Polym. Sci.* **1994**, *52*, 617.
19. St-Pierre, N.; Favis, B. D.; Ramsay, B. A.; Ramsay, J. A.; Verhoogt, H. *Polymer* **1997**, *38*, 647.
20. Sailaja, R. R. N.; Chanda, M. *J. Appl. Polym. Sci.* **2001**, *80*, 863.
21. Sabetzadeh, M.; Bagheri, R.; Masoomi, M. *J. Appl. Polym. Sci.* **2012**, *126*, E63–E69.
22. Ratanakamnuan, U.; Aht-Ong, D. *J. Appl. Polym. Sci.* **2006**, *100*, 2717.
23. Sathe, S. N.; Rao, G. S. S.; Devi, S. *J. Appl. Polym. Sci.* **1994**, *53*, 239.

24. Vermeesch, I.; Groeninckx, G. *J. Appl. Polym. Sci.* **1994**, *53*, 1365.
25. Gaylord, N. G.; Mehta, M. *J. Polym. Sci. Polym. Lett. Ed.* **1982**, *20*, 481.
26. Liu, W.; Wang, Y. J.; Sun, Z. *J. Appl. Polym. Sci.* **2003**, *88*, 2904.
27. John, J.; Bhattacharya, M. *Polym. Int.* **1999**, *48*, 1165.
28. Sugih, A. K.; Drijfhout, J. P.; Picchioni, F.; Janssen, L. P. B. M.; Heeres, H. J. *J. Appl. Polym. Sci.* **2009**, *114*, 2315.
29. Kerner, E. H. *Proc Phys Soc* **1956**, *69B*, 808.
30. Nielsen, L. E. *Mechanical Properties of Polymers and Composites*. Marcel Dekker: New York, **1974**.
31. Nicolais, L. N. M. *Polym. Eng. Sci.* **1971**, *1*, 194.
32. Pedroso, A. G.; Rosa, D. S. *Carbohydr. Polym.* **2005**, *59*, 1.
33. Walia, P. S.; Lawton, J. W.; Shogren, R. L. *J. Appl. Polym. Sci.* **2002**, *84*, 121.
34. Willemse, R. C.; de Boer, A. P.; van Dam, J.; Gotsis, A. D. *Polymer* **1998**, *39*, 5879.
35. Bikiaris, D.; Panayiotou, C. *J. Appl. Polym. Sci.* **1998**, *70*, 1503.
36. Veenstra, H.; Verkooijen, P. C. J.; van Lent, B. J. J.; van Dam, J.; de Boer, A. P.; Nijhof, A. P. H. *J. Polymer* **2000**, *41*, 1817.
37. Manas-Zloczower, I. *Rheol. Bull.* **1997**, *66*, 5.
38. Shin, B. Y.; Jang, S. H.; Kim, B. S. *Polym. Eng. Sci.* **2011**, *51*, 826.
39. Bier, J. M.; Verbeek, C. J. R.; Lay, M. C. *J. Ther. Anal. Calorimetry* **2012**, 1–13.
40. Khonakdar, H. A.; Wagenknecht, U.; Jafari, S. H.; Hässler, R.; Eslami, H. *Adv. Polym. Technol.* **2004**, *23*, 307.
41. Popli, R.; Glotin, M.; Mandelkern, L.; Benson, R. S. *J. Polym. Sci. Polym. Phys. Ed.* **1984**, *22*, 407.