

Mechanical Properties of Protein-Based Polymer Blends

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Abstract: *This study investigated the compatibilisation of Novatein® Thermoplastic Protein (NTP) blends with other polymers. NTP was blended with two different types of polymers: a petroleum-based polyolefin (low-linear density polyethylene, LLDPE) and a biodegradable synthetic polyester (polybutylene succinate, PBS). It was a relatively straightforward process to produce a compatible blends of LLDPE and PBS with NTP regardless of the obvious difference in chemical structure between these polymers. The goals of the study were to develop an understanding of interactions between NTP and other polymers that influences the mechanical properties and the performance of the blends were evaluated in light of mathematical modeling.*

Keywords: Blood meal, LLDPE, PBS, biodegradable, compatibility, blending

1. INTRODUCTION

Recent developments of biodegradable polymers have greatly been driven by a desire to replace synthetic plastics. More recently, Novatein® Thermoplastic Protein (NTP) have been developed from by-products of animal rendering (blood meal) which do not compete with human food, such as raw materials used for biofuel production.¹ NTP is currently being commercialised by Aduro Biopolymers LP.² Blood meal, a dry inert powder made from blood is used as a high-nitrogen fertiliser and a high protein animal feed. It is one of the highest non-synthetic sources of nitrogen coming from meat processing. Blood meal is different from meat bone meal in that blood meal contains a much higher amount of nitrogen, while meat bone meal contains phosphorus.

Transformation of blood meal into Novatein Thermoplastics (NTP) involves addition of additives. The additives are water, a protein denaturant (urea), a reducing agent (sodium sulfite, SS) and a surfactant (sodium dodecylsulfate, SDS).^{3,5} These additives break covalent crosslinking and reduce hydrophobic and hydrogen bonding between chains and allow the formation of new interactions after processing. The resulting material consolidates during extrusion, and can be injection moulded and formed into products. Products that

can be produced from protein-based thermoplastics include seedling trays, biodegradable plant pots, vine clips, containers and pegs.

NTP is easily composted due to the hydrophilic nature of protein. It is sensitive towards moisture, capable of breaking down in a matter of weeks in high humidity, or even days when immersed in water. This makes NTP an ideal starting material as biodegradable-based polymers especially in polymer blends.⁴ However, the mechanical properties of NTP are not exceptional. One of the most apparent limitations of NTP is brittleness. Although water is an efficient plasticiser to increase toughness, during production and storage, water desorbs from the moulded plastic over time and makes the materials brittle. TEG has been used as plasticiser in addition to water, but it has been shown that the tensile strength and the modulus of the materials are lower than desirable.⁶

Blending is an interesting option that offers the possibility to develop new materials with more desirable properties. Among the reasons for the popularity of polymer blends is the versatility in tailoring the end products' properties; whether to produce synergistic combinations of two components, such as high modulus and toughness, improving water-resistance, biodegradability and recycling or to lower costs. For instance, in the packaging industry, excellent mechanical properties are required as well as, for example water-resistance. The hydrophilic nature of NTP could potentially be manipulated by blending it with hydrophobic polymers, offering an excellent combination of mechanical properties from two different polymers whilst maintaining some of its biodegradation. Although the rate of decomposition of the materials might be compromised, optimal formulation in terms of composition could minimise these concerns.

However, polymer blending is one of those things that are "easier said than done". Developing miscible blends has been proven to be a daunting task where the principal challenges include the variability in the morphology obtained, possible reduction in thermal stability and mechanical properties. This study was done to explore the potential of blending NTP with other thermoplastics using extrusion to improve NTP's mechanical properties. The objective of this study was to investigate the influence of blending NTP with two different types of polymers: (1) blending with LLDPE and (2) blending with PBS. Here, LLDPE and PBS was chosen because it has a similar range of processing conditions to NTP. Modeling of mechanical properties were also performed and correlated to observed values and the performance were evaluated.

2. EXPERIMENTAL

2.1 Materials

Bloodmeal was supplied by Wallace Corporation (New Zealand) and sieved to an average particle size of 700 μ m and was mostly bovine with some chicken blood. Technical grade sodium dodecyl sulfate (SDS) and analytical grade sodium sulfite (SS) were purchased from Biolab NZ and BDH Lab Supplies. Agricultural grade urea was obtained from Balance Agri-nutrients (NZ). Low linear density polyethylene (LLDPE) grade Cotene 3901 and polybutylene succinate (PBS) was purchased from J. R. Courtenay and Showa High Polymer, Injection moulding grade #3020, respectively.

2.2 Preparation of Novatein Thermoplastics Protein (NTP)

NTP was prepared by dissolving urea (20 g), SDS (6 g), and sodium sulphate (6 g) in water (80 g). The solution was heated until the temperature reached 50°C–60°C followed by blending with bloodmeal powder (200 g) in a high-speed mixer for 5 min. The mixtures were stored at < 5°C for at least 24 h prior to extrusion. Extrusion was performed using a ThermoPrism TSE-16-TC twin screw extruder at a screw speed of 150 rpm and temperature settings of 70°C, 100°C, 100°C, 100°C and 120°C from feed to exit die (Figure 1).

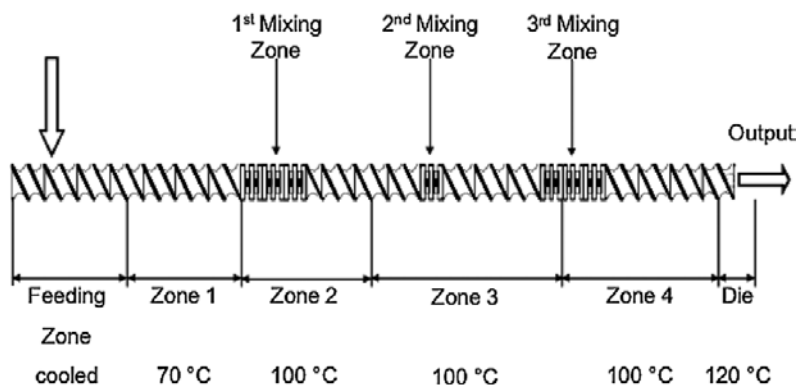


Figure 1: Extruder screw configuration with temperature profile.

The screw diameter was 16 mm at L/D ratio of 24:1 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 extruded NTP was granulated using tri-blade granulator from Castin Machinery Manufacturer Ltd., China.

2.3 Extrusion

NTP with LLDPE or PBS and were mixed in a plastic zip-lock bag prior to 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°C, 100°C, 100°C, 100°C and 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.

2.4 Injection Molding

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

2.5 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, elongation at break and Young's modulus were analysed for conditioned samples.

2.6 Modeling Mechanical Properties

The behaviour 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 equation⁷:

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

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 Equation 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 modulus of polymer blends generally in range between an upper bound, E_u , given by the parallel model (Equation 3) and a lower bound, E_L , given by the series model (Equation 4):

$$E_u = \phi_1 E_1 + \phi_2 E_2 \quad (3)$$

$$\frac{1}{E_L} = \frac{\phi_1}{E_1} + \frac{\phi_2}{E_2} \quad (4)$$

in which E_i and ϕ_i are the modulus and volume fraction of phase i . These models are frequently used as limiting models regardless of morphology.

The elongation at break for polymer and composites can be evaluated using Nielsen model.⁸ 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. For good adhesion between phases, the following Nielsen equation is approximately correct:

$$\varepsilon_c = \varepsilon_0 \left(1 - \phi^{1/3} \right) \quad (5)$$

$$\sigma_c = \sigma_m (1 - 1.21\phi^{2/3}) \quad (6)$$

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 Narkis⁹ assuming no adhesion between phases and failure is at the filler–matrix interface. In Equation 6, σ_c is the composite's tensile strength and σ_m is the polymer matrix's tensile strength. In this study, NTP was blended with LLDPE in different

proportions. The effect of matrix filler amount were analysed in light of mechanical properties.

3. RESULTS AND DISCUSSION

3.1 Mechanical Properties

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.

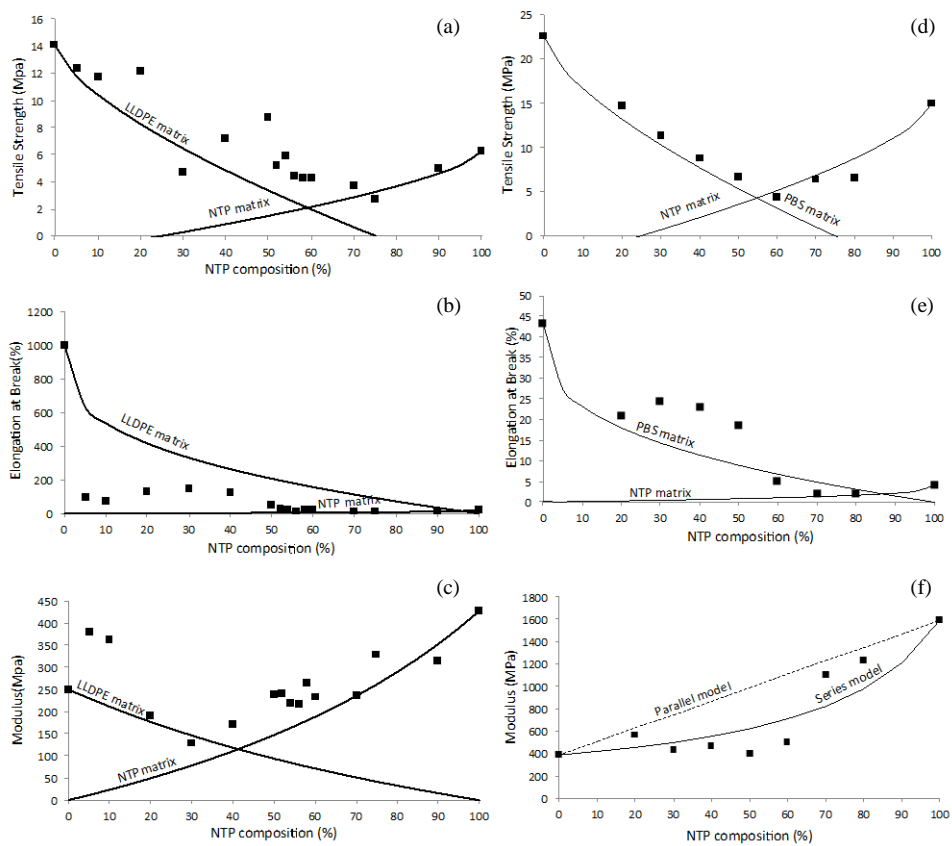


Figure 2: Mechanical properties of NTP/LLDPE (a, b, c) blends and NTP/PBS blends (d, e, f). Relevant models also included using either NTP or LLDPE as matrix.

The tensile strength of NTP/LLDPE blends decreased with increasing NTP contents (Figure 2). 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 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. The theoretical values of tensile strength have been calculated using the Nicolais-Narkis model, which assumes no adhesion between NTP and LLDPE. Experimental values was significantly higher than theoretical value.

Elongation at break for experimental values of NTP/LLDPE blends 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. Elongation at break calculated from the Nielsen model is plotted in Figure 2. The Nielsen model did not show agreement with experimental values, except at high NTP content.

In the Kerner model, poor interfacial adhesion is assumed and most successfully described Young's Modulus using NTP as matrix. A sharp drop in modulus was observed with the inclusion of NTP, but increased with increasing NTP content above 50 wt % NTP. 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.

For tensile strength of NTP/PBS blends (Figure 2d), it was apparent that the tensile strength generally decreased with increasing NTP content. At 60 NTP/40 PBS, the tensile strength dropped to about 70% lower than pure PBS. In general, the tensile strength of the blends was below that of pure NTP, suggesting that adhesion between the two phases was very poor. This was also supported by the Nicolais-Narkis model, which assume that there is no adhesion between the spherical fillers with matrix if the fracture goes through the filler-matrix interface.

The addition of NTP decreased the elongation at break of blends (Figure 2e). At 70% NTP, the elongation at break dropped below the elongation at break of pure NTP. Considering that NTP is much more brittle than PBS (5% vs. 43%), the result is not surprising and is similar to what is expected of particulate composites. Poor interfacial adhesion or introduction of a dispersed phase into a matrix typically causes a dramatic decrease in elongation at break. Despite the poor adhesion, PBS can still elongate significantly at lower NTP content (< 50%). However PBS gets constrained by NTP at higher NTP content, resulting in a significantly lower elongation at break comparable to that of NTP. Blends of NTP/PBS showed a better elongation at break when compared with NTP/LLDPE blends. It was postulated that blending NTP with PBS which is a biodegradable synthetic polyester as compared to a petroleum-based polyolefin (LLDPE) lead to a better compatibility between two phases. This is shown in morphology section. The modulus of NTP/PBS blends increased with increased NTP content. NTP has a higher modulus than PBS and the trend appeared similar to what would be expected using the mixing rule of series and parallel model for polymer blends. These results would be consistent to what is expected when including rigid particles into a soft PBS matrix. The increase in modulus was mostly unaffected by poor adhesion, contrary to what was observed for tensile strength.

3.2 Morphology

Figure 3 presents the morphology of NTP/LLDPE and NTP/PBS blends at 50% NTP composition. Using different polymer in blends had drastically change the morphology. In NTP/LLDPE blends, two distinct phases were observed. The incompatibility between the two polymers was suspected to lead to large domains of NTP particles suspended in a weak matrix of mostly LLDPE. In NTP/PBS blends, NTP particles was evenly distributed that the blend formed two phases, a NTP rich and a PBS rich phase. Despite the poor adhesion, observed by mechanical testing, PBS can still elongate significantly at 50% NTP content resulting to a better elongation at break properties when compared to Nielsen model.

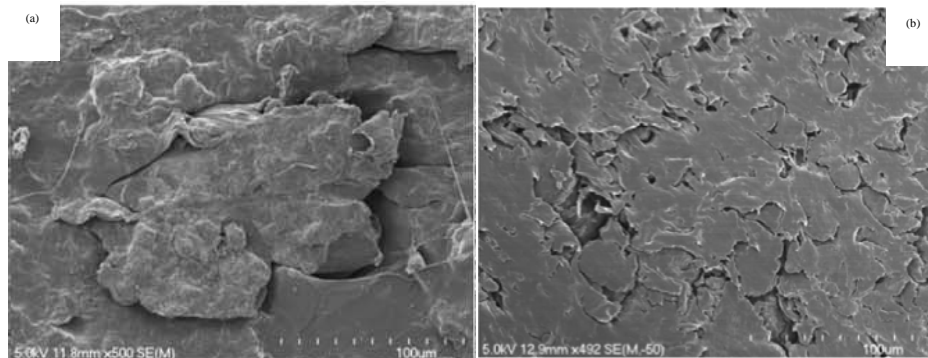


Figure 3: Morphology of (a) NTP/LLDPE and (b) NTP/PBS blends at 50% composition.

4. CONCLUSION

NTP was successfully blended with LLDPE and PBS using extrusion and injection moulding. In term of processing, none difficulties were encountered when blending more NTP amount in LLDPE and PBS blends. This observation is important which showed high potential of NTP in developing NTP blends as starting material. This is because excessive aggregation of the protein usually occurred during thermal event. With regard to performance evaluation, specifically in mechanical properties, blending NTP with other polymers resulted in an immiscible blend and poor interfacial adhesion between the two very distinct phases of different polymers. However, the combining effect between two polymers showed an encouraging results, for example, LLDPE is not biodegradable but has an exceptional elongation at break. By blending LLDPE with NTP, a reduction in the brittleness of NTP can be expected. The potential of blending NTP with a synthetic biodegradable polymer (PBS) was also assessed with the motivation to produce a completely biodegradable blend and the mechanical properties and morphology were found promising. At 50% NTP composition, PBS can still elongate and formed evenly two phases distributed blends.

5. REFERENCES

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