

# Properties of Blends of Novatein Thermoplastic Protein from Bloodmeal and Polybutylene Succinate Using Two Compatibilizers

K. I. Ku Marsilla and C. J. R. Verbeek

**Abstract**—The use of dual compatibilizers, poly (2-ethyl-2-oxazoline) (PEOX) and polymeric methylene diphenyl diisocyanate (pMDI) in Novatein thermoplastic protein from bloodmeal (NTP) and PBS blends were investigated. A composition of 50% of NTP was used for all formulations with different percentage compatibilizer. Mechanical, morphology, thermal and water absorption were used as analysis methods to study blend properties. To improve compatibility, two different approaches to blending the compatibilizers were used. Firstly, PEOX was added before extrusion this has improved the blend's tensile strength. Secondly, addition of PEOX during NTP production followed by pMDI added before injection molding, showed a further improvement in tensile strength. SEM revealed that PEOX has improved the dispersion of NTP and pMDI has strengthened the adhesion between phases consistent with mechanical property results. A broad  $\tan \delta$  peak in DMA analysis was obtained indicated improved compatibility in blends using two compatibilizers. In spite of that, the addition of dual compatibilizer has reduced the water resistance of PBS.

**Index Terms**—Blends, bloodmeal, compatibilizer, PBS

## I. INTRODUCTION

In the research of sustainable material from non-potential food sources, bloodmeal is one of the best candidates for bioplastic manufacture. It is one of the highest non-synthetic sources of nitrogen coming from meat processing. Approximately 80 000 tonnes of raw blood is collected annually in New Zealand is dried and sold as low cost animal feed and fertilizer. Novatein Thermoplastic Protein (NTP) is a new developed material from bloodmeal by Novatein Bioplastic Technologies in Hamilton, New Zealand [1], [2]. Previous research by Verbeek and van den Berg [3]-[5] showed that dry processing techniques, such as extrusion and injection moulding were successfully used to produce NTP with good mechanical properties.

From the plastic industry's point of view, development of improved blended materials with a full set of desired properties is much more effective and cheaper method compared with synthesized of new polymers [6] and [7]. NTP often present processing difficulties because of their hydrophilic nature. Denaturing of proteins under thermal and mechanical process also has lead to unsatisfactory mechanical properties such as brittleness. Therefore, blending NTP with other polymers may offer a solution to these problems.

However, most blends are immiscible. The process conditions are challenging because of dissimilar nature of natural and synthetic polymer, thus requiring compatibilization to achieve good performance.

A compatibilizer is widely used as a third component to improve the compatibility between blended polymers. Strategies for compatibilization listed by L. A. Utracki includes addition of a third component that is miscible with both phases or addition of copolymers that has one part miscible with one phase and another with the another phase [8]-[11]. The copolymer layer makes a strong mechanical interface by forming entanglements with the homopolymer bulk phases [12]. Polymers modified by this technique have nucleophilic end-groups such as carboxylic acids, anhydride, amine or hydroxyl groups. These groups then form covalent bonds with suitable electrophilic functional groups, such as epoxide, oxazoline, isocyanate or carboimide, which turns the incompatible blend into a compatible and useful material [13].

Anhydride groups were found very effective in improving compatibility and strength of soy protein and polyester blends [14]. Enhanced mechanical strength was achieved for polybutylene succinate (PBS) at 65% soy isolate and 5% of maleic anhydride grafted PBS [14]. MA-grafted PLA with 0.65% MA in corn starch displays improved PLA/starch interfacial adhesion compared with uncompatibilized blends.

Other than that, it was found that carboxyl groups and or amino groups functionality in proteins are capable to react with oxazoline functional groups. Okada and Aoi [15] prepared novel chitin derivatives using poly (2-alkyl-2-oxazoline), poly (2-methyl-2-oxazoline) and poly (2-ethyl-2-oxazoline)(PEOX) under mild conditions at 27°C in dimethyl sulfoxide (DMSO). The result showed improved solubility in organic solvents. Takasu *et al.* [16] developed blends of PVA/chitin-g-poly (2-ethyl-2-oxazoline) and found that covalent linked compatibilizer exhibited miscibility with PVA. It is not only interacts with PVA but destructed the crystal structures of chitin and improved it's solubility. PLA has also been blended with SPI and SPC and it was found that PEOX has increased the tensile strength, reduced particle size and reduce water absorption [17].

Polymeric methylene diphenyl diisocyanate (pMDI) was found highly reactive with hydroxyl functional group to form urethane linkages [18] and residues of untreated MDI are not expected in a blend due to high reactivity of isocyanate groups [19]. Synergetic effect of mechanical properties was observed in PLA and starch blends using MDI as compatibilizer [19], [20]. Soy protein isolate (SPI) and PCL blends compatibilized

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with MDI has also improved the mechanical properties and water resistance of the blends [21]. Liu B. *et al.* reported a synergetic effect of dual compatibilizers by using both PEOX and pMDI in PLA and soy protein concentrate (SPC). The addition of compatibilizers into PLA/SPC blends reduced SPC inclusion size and increased interfacial bonding between PLA and SPC, which reduced stress concentration and promoted stress transfer at the interface as well as increased the tensile strength [22].

Synthetic and microbial polyesters produce a wide range of biodegradable polymers. These materials can be synthesized by polycondensation of the hydroxyl acid or by ring opening polymerization [23]. Biodegradable polyesters such as polycaprolactone (PCL), polybutylene succinate (PBS), polyhydroxybutyrate (PHA) and polylactic acid (PLA) have been developed commercially and currently available on the market. PBS, also known as BIONOLLE, is succinic acid-based biodegradable aliphatic polyesters which is synthesized by condensation polymerization of succinic acid with 1,4-butanediol and ethylene glycol. The advantages observed are excellent biodegradability, thermoplastic processability and balanced mechanical properties. Despite its good performance, many efforts have been made to modify PBS-based materials to reduce the cost. In this study, PBS has been chosen because of its melting point was in the same region as NTP. Blends of PBS and NTP were prepared with incorporation of different compatibilizer. Considering the high cost of PBS, NTP compositions were set at 50% for all samples. Effects of different compatibilizers content and compatibilizer loading techniques on mechanical, thermal, morphology and water absorption were studied.

## II. METHODOLOGY

### A. Materials

Bloodmeal was supplied by Wallace Corporation (New Zealand) and sieved to an average particle size of 700  $\mu\text{m}$ . Technical grade sodium dodecyl sulfate (SDS) and analytical grade sodium sulfite were purchased from BiolabNz and BDH Lab Supplies. Agricultural grade urea was obtained from Balance Agri-nutrients (NZ). Poly (phenyl isocyanate)-co-formaldehyde (pMDI) and poly-2-ethyl-2-oxazoline (PEOX) were obtained from Sigma Aldrich and were used as received.

### B. Preparation of Novatein Thermoplastic Protein (NTP)

Samples were prepared by dissolving urea (20 g), sodium dodecyl sulphate (6 g) and sodium sulphate (6 g) in water (80 g). 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 minutes. The mixtures were stored for at least 24 hours 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 70,100,100,100,120°C from feed to exit die. The screw diameter was 16mm 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 extruded NTP was granulated using tri-blade granulator from

Castin Machinery Manufacturer Ltd., New Zealand.

### C. Preparation of Blends (NTP/PBS)

PBS was extruded with NTP and was granulated. Compatibilizer was added to the blends and was extruded again at the same parameters setting with NTP. Standard tensile bars (ASTM D638) were prepared using BOY 35 A Injection Moulding Machine with temperature profile of 110,115,120,120,120°C from feed to exit die zone. Table I presented the formulations of NTP/PBS blends. NP<sub>0/0</sub> is a blend without compatibilizer. pMDI was added as a compatibilizer before extrusion for sample NP<sub>7/0</sub>. In the case of two compatibilizers, PEOX was added while extrusion process while pMDI was added before injection moulding (NP<sub>7/3</sub>). For sample NP<sub>7/3\*</sub>, PEOX was dissolved in water before adding urea, sodium dodecyl sulphate and sodium sulphate. The specimen were conditioned in conditioning chamber at 23°C and 50% relative humidity, equilibrating to ~10% moisture content.

TABLE I: FORMULATIONS OF NTP/PBS BLENDS

Sample Name	NTP (wt%)	PBS (wt%)	pMDI (wt%)	PEOX (wt%)	PEOX (pph) dissolve in NTP formulation
PBS	0	100	0	0	0
NP <sub>0/0</sub>	50	50	0	0	0
NP <sub>7/0</sub>	50	43	7	0	0
NP <sub>7/3</sub>	50	40	7	3	0
NP <sub>7/3*</sub>	50	43	7	0	3
NTP	100	0	0	0	0

Formulations

### D. Mechanical Testing

Tensile specimens were tested using Instron model 4204 according to ASTM D638-86 test procedure. For each experiment five specimens were conditioned at 23°C and 50% relative humidity, equilibrating to ~10% moisture content. Tensile strength, elongation at break and secant modulus between 0.0005 – 0.0025 were analyzed for conditioned samples.

### E. Morphology

The microstructures of NTP/PBS were investigated using a scanning electron microscopy (SEM) Hitachi S-4700. Fracture surfaces were sputter coated with platinum before scanning. An accelerating voltage of 5kV was applied.

### F. Dynamic Mechanical Analysis

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

### G. Water Absorption

All samples were oven dried at 80°C until constant weight. Dried samples were immersed in water at room temperature. Samples were removed from water, blotted with a tissue paper

to remove excess water and then weighed. The water absorption was calculated on a dry sample weight basis.

### III. RESULTS AND DISCUSSIONS

#### A. Mechanical Properties

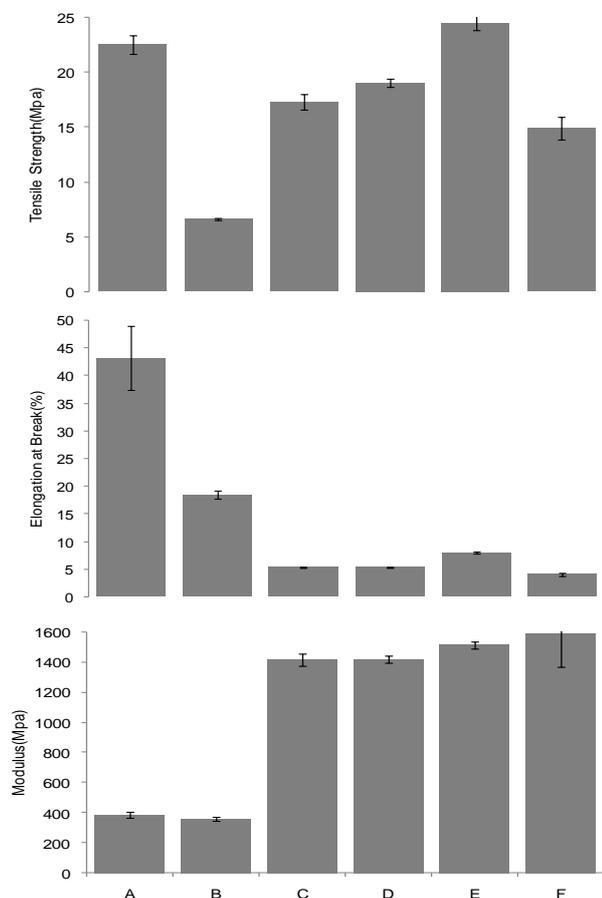


Fig. 1. Tensile strength, percent elongation and secant modulus of NTP/PBS blends [ A:PBS; B:NP 0/0; C:NP 7/0; D:NP 7/3 E:NP 7/3\* F: NTP ]

Fig. 1 presented the tensile strength, percent elongation and secant modulus of various NTP/PBS blends. The tensile strength of blends with compatibilizers (C, D and E) were higher compared to blends without any compatibilizer (B) but the elongation at break showed an opposite trend. The percentage elongation of pure PBS was decreased over 50% after blending with NTP and decreased to 5-7% after compatibilizers were added. Blends with compatibilizer showed brittle properties and the modulus approached that of pure NTP. Tensile strength of NP<sub>7/0</sub> showed almost a three full increase compared to blends without compatibilizer. This indicates that pMDI has improved the adhesion between NTP and PBS. Meanwhile, because of the interactions and entanglement between phases were strong, it might have restricted the movement of polymer chains thus decreased the elongation at break properties.

The tensile strength of NP<sub>7/3\*</sub> was higher compared to NP<sub>7/3</sub>. A slight increase in elongation at break was also observed. The difference between these two samples was the blending techniques of PEOX. Apparently, the techniques of blending play an important rule in mechanical performance. The

addition of PEOX in NTP formulation was more effective than adding it at extrusion process. It has been reported that carboxylic acid end groups of PBT could easily react with oxazoline functional groups in the melt state [24]. The reaction between the carboxylic and oxazoline groups result in an ester-amide linkage and it is a fast reaction [25].

Isocyanate (NCO) groups in pMDI can react with amines, carboxylic acids or hydroxyl containing polymers while oxazoline groups in PEOX can react with either amines or carboxylic acids end groups or acid end groups of polyesters. The chemical reactions between these groups are presented in Fig. 2. Protein (NTP) has amino and carboxyl groups that could potentially react with the compatibilizers. Therefore, the reaction between PBS and NTP could be formed by those compatibilizers.

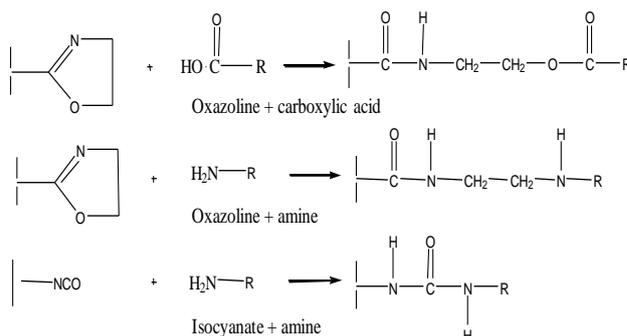


Fig. 2. Chemical reactions between functional groups and and polymer end groups1

Y. D. Li *et al.* found that NCO groups prefer to react with NH<sub>2</sub> groups of soy protein isolate (SPI) rather than OH groups. Other than that, pMDI also has high reactivity towards water. Considering these, to avoid the extreme situation that pMDI will react only with water and NH<sub>2</sub> in NTP and prevent reactions with PBS, NTP and PBS were extruded first the compatibilizers were added later. Experiment blends of NTP and PBS with compatibilizers added before extruding showed poor mechanical properties and were lower than the tensile strength of blends without compatibilizer (results were not presented in this paper). These findings suggested that PEOX was expected to interact with the carboxyl end in NTP, resulting in a finer dispersion and when pMDI was added, the NCO groups prefer to react with amines in NTP as mentioned above, thus strong interactions between the compatibilizers with both amines and carboxyl groups in NTP exhibit the synergetic effect in tensile strength.

It is expected that morphology must be the determining factor to explain this behavior. According to literature, PEOX has the capability of reducing particle sizes resulting in finer structure, although not showing great improvement in tensile strength [17], [22]. Research of PLA/soy protein blends using dual compatibilizer (PEOX and pMDI) proved that the addition of compatibilizers into the blends reduced SPC inclusion size and increase tensile strength to higher than that of pure PLA [22]. In our findings, the dispersion of particle of NTP was better when PEOX was added to the system and will be discuss later in the morphology section.

#### B. Morphology

The morphology of blended materials is one way to study

property-structure relationships. Behavior of polymers blends such as particle size, phase morphology, the dispersion and distribution of particles, and fracture pattern can be observed. Fig. 3 shows the morphology of compatibilized blends of NTP/PBS at different magnifications. From Fig. 3 (A), the addition of pMDI revealed at least two agglomerated phases. This confirmed that isocyanate groups interacted with both NTP and PBS. In Fig. (B) two compatibilizers were used, showed that one phase is NTP rich and the other is PBS rich. There are no voids observed while NTP was encapsulated in the PBS matrix. Good adhesion between phases can be seen at high magnification. This kind of change in morphology was reflected in a better tensile strength as explained earlier. Comparing with Fig. 3 (C), very little phase separation was observed. Fig. 4 shows NTP phases without PEOX (i) and with PEOX (ii). By dissolving PEOX in NTP formulations, it has improved the dispersion of NTP and it was found that pMDI has strengthened the interfacial adhesion of the blends. This finding was consistent with previous work [22].

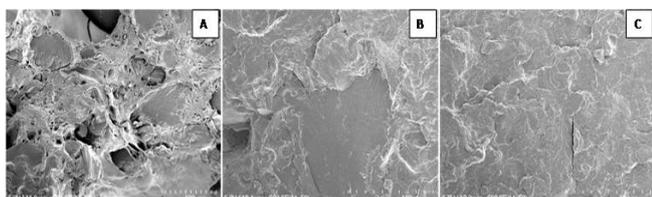


Fig. 3. Morphology of NTP/PBS compatibilized blends A: NP 7/0, B: NP 7/3, and C: NP 7/3\*

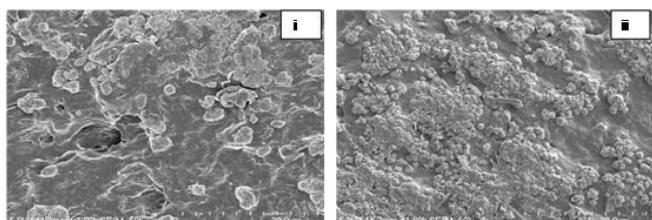


Fig. 4. NTP particles without any PEOX (i), NTP with PEOX dissolved in water prior to extrusion (ii)

### C. DMA Analysis

Storage, loss modulus and  $\tan \delta$  of NTP/PBS blends are shown in Fig. 5. Referring to the storage modulus graph, the modulus continually decreased as temperature increased. The sudden decrease was at approximately  $-35^\circ\text{C}$  and is in agreement with loss modulus and  $\tan \delta$  indicating a glass transition temperature. It can be seen that modulus of blend without compatibilizer (b) was below modulus of PBS while blends with compatibilizers (c, d, and e) showed a higher modulus. The peak at  $\tan \delta$ , interpreted, as glass transition was not significantly shifted however reduced intensity to a broad peak for compatibilized blends were observed. It indicates that the mobility between polymer chains were restricted and improved compatibility were obtained consistent with earlier results in mechanical properties section.

### D. Water Absorption

Table II presents the results of water absorption test of blends over 5 days. Water absorption characteristic is very important in bioplastic applications. One of major challenges using natural polymer is to increase its water resistant. From the table, NTP itself absorbs about 90% of water while PBS

absorbs 0.91%. Without any compatibilizer, the water absorption of NTP has been improved to about 18.78% when blended with PBS. However, the addition of compatibilizers has reduced the water resistant of PBS to about 8%. Considering that the blends have 50% of NTP that is hydrophilic in nature, reduction of 8% was reasonable although this may narrow down the application window of the blends. NP 7/0 exhibit the lowest water uptake indicates that pMDI is less reactive towards moisture and water compared to blends contained PEOX. Other research found that reactions of pMDI with functional groups in SPC decreased the water absorption by polarity reduction in SPC where at the same time increased its wetting by PLA [22].

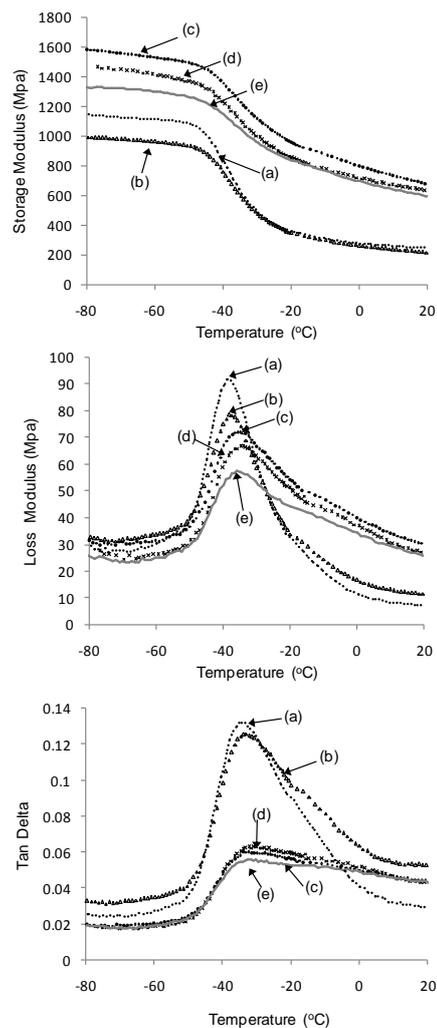


Fig. 5. Temperature dependence of storage modulus, loss modulus and tan delta of NTP/PBS blends; (a) PBS; (b)NP 0/0; (c)NP 7/0; (d):NP 7/3; (e)NP 7/3\*

TABLE II: WATER ABSORPTION OF BLENDS OVER 5 DAYS

Blends	Water absorption (wt%) over 5 days
100 PBS	0.91
NP 0/0	18.78
NP 7/0	5.333
NP 7/3	8.48
NP 7/3*	7.57
100 NTP	90.42

#### IV. CONCLUSION

50 % blends of NTP/PBS were successfully prepared using twin screw extrusion and injection moulding. Different ways of compatibilizer blending has significantly improved the tensile strength of the blends. Dissolving PEOX in water prior to NTP extrusion was found to be most effective. The tensile strength of this sample has been improved to above of the tensile strength of pure PBS. DMA analysis results was found consistent with mechanical properties results where tan delta peak of compatibilized blends was reduced to a broad peak probably due to restricted mobility of the PBS polymer chains. Indeed the  $T_g$  were not significantly shifted. Compatibilized blends showed less water absorption compared to uncompatibilized blend although it has reduced the water resistant properties of pure PBS.

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