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Foaming Behavior of Novatein and Blends with Polyethylene Compatibilised by Maleic Anhydride

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Abstract. Novatein® thermoplastic protein (NTP), a bloodmeal based thermoplastic, was successfully foamed without blowing agent or blending with other polymers using a BOY-35A injection moulder in free expansion mode. Previously, only soy protein has been successfully continuously foamed and zein and gluten batch foamed without blending or rheological modification. The greatest expansion ratio for NTP was 4.4 at 165°C. Blending NTP with compatibilised LLDPE and LDPE and adding blowing agent reduced expansion ratios. The foams exhibited a fibrous nature, with cell structures similar to those reported in literature for extrusion foamed thermoplastic soy protein isolate. SEM pictures suggested a possible role of either sodium sulphite, sodium dodecyl sulphate or sodium sulphate as a nucleating agent as particulates were found on the cell surfaces. Triethylene glycol and urea were thought to contribute to NTP foaming, along with water present in NTP, with two or more acting as the blowing agent.

Keywords: Free Expansion Foaming, Single Screw, Protein Bio-polymer, Polyethylene, Compatibilised Blend
PACS: 82.35.Pq, 83.80.TC, 83.80.Iz, 81.20.Hy

INTRODUCTION

The waste disposal problems of using non-biodegradable foamed polymeric materials in short-term/limited-life applications such as packaging has resulted in increased use of biodegradable, bio-derived and protein based thermoplastics. One potential biodegradable, protein based thermoplastic is Novatein® Thermoplastic Protein (NTP), developed from bloodmeal by the University of Waikato and Aduro Biopolymers, New Zealand. Bloodmeal is plasticized by adding urea, sodium sulphite, sodium dodecyl sulphate, water and triethylene glycol, and extruded to produce a consolidated thermoplastic with similar mechanical properties to linear low density polyethylene.

Only a small number of thermoplastic proteins have been successfully foamed using extrusion. Examples include soy protein isolate which was successfully foamed into sheets at 150-160°C [1], blends of pearl millet flour and zein (30:70) foamed at 105°C [2], and blends of soy protein concentrate and polylactic acid (PLA) at 150-160°C [3]. In all cases, an additional chemical blowing agent was employed to promote foaming. In comparison, injection foaming is usually conducted into a mould and either a short shot or core pull is used to enable the required expansion. Injection foaming has been applied to a wide range of biopolymers including PLA, PHBV, PBAT and starch [4], however it has only been applied to one other protein thermoplastic (soy) [5].

Previously, the extrusion foaming ability of NTP blended with compatibilised linear low density polyethylene (LLDPE) was investigated using the internal moisture content and sodium bicarbonate as the blowing agent [6]. Two twin screw extruders were used with 10 mm diameter dies. Expansion ratios of < 2 were observed and foam morphology consisted of large irregular closed cells up to 2 mm in size. A foaming grade LDPE was also tried with NTP. While the material was expected to foam better when compared to using LLDPE, because of its different melt flow index and strain hardening behavior, no difference in foaming ability of the blends was observed at 120°C. The low expansion ratios were attributed to the significant losses of blowing agent through the feed hopper and to gases escaping through the unconsolidated material at the die.

To prevent the loss of gases and improve foaming, this work explored the use of a single screw BOY 35A injection moulder in free expansion mode for extrusion foaming. The foaming ability of NTP, LDPE, LLDPE and 50:50 blends was explored over a temperature range of 150-165°C. The materials, blends and resulting foams were characterized by examining cell morphology and expansion ratios.

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MATERIALS AND METHODS

Pre-extruded NTP (PNTP) was prepared in a Labtech bench scale high speed mixer at 1400 RPM by blending bloodmeal with a denaturing solution and triethylene glycol as a plasticizer. The denaturating solution was prepared by dissolving sodium sulphite (SS), sodium dodecyl sulphate (SDS) and urea in water by heating and agitation (**TABLE 1**). This solution was added to the bloodmeal in the high speed mixer in two stages with two minutes of mixing between additions. The plasticizer component was then added in the same manner. The PNTP was then stored overnight at 4 ℃ in a zip lock bag until extrusion.

TABLE 1: Pre-extruded NTP composition

	Reagent	Source	Grade	Weight (g)
Protein Source	Bloodmeal (< 710 μm)	Wallace Corporation Limited, NZ	Agricultural	1500
Denaturing Solution	Water	Produced on-site	Distilled	600
	Sodium Sulphite	Merck, Germany	Analytical	45
	Sodium Do-decyl Sulphate	Merck, Germany	Synthesis	45
	Urea	Ballance Agri-Nutrients, NZ	Agricultural	150
Plasticiser	Triethylene Glycol	Merck, Germany	Industrial	300

Consolidated NTP was produced by extruding PNTP using a Labtech Scientific Twin Screw Extruder across a temperature profile from feed to die of 70,100,100,110,120°C. This extruder has an L/D ratio of 40, 26 mm diameter screws and was operated at a torque of 55-60%. The extruded material (ENTP) was then granulated to a size of less than 4 mm using a tri-blade granulator from Castin Machinery (NZ).

The ENTP and the polyethylene phase (either LLDPE or LDPE) was then extruded with polyethylene grafted maleic anhydride (PE-g-MAH) compatibiliser (10 % on a weight basis). Cotene 3901 (Elastochem, NZ) with a melt flow index (MFI) of 4.0 g/10 min and annealed density of 0.905 g/cm³ was used for LLDPE. LDPE used was Lotrene FD0274 (MFI of 2.4 g/10 min) commonly used for foamed polyethylene products. This material was supplied by Interplas Agencies Limited via Nulon Limited, Auckland, New Zealand. PE-g-MAH was supplied by Sigma Aldrich (CAS 9006-26-2).

Following the second extrusion the material was granulated to less than 4 mm for foaming in the BOY 35A injection moulder. The single screw has a diameter of 24 mm and an L/D ratio of 22. The machine was operated by withholding the die from the mould to enable free expansion of the material.

The foaming behavior of NTP, LDPE, a 50:10:40 blend of NTP: PE-g-MAH:LDPE blend, LLDPE and a 50:10:40 LLDPE blend was investigated in this study with respect to temperature and sodium bicarbonate content (**TABLE 2**). Temperature profiles of 100, 125, X, 135 and 125 °C from feed to die were investigated for foaming where temperature X was set to either 150, 155, 160 or 165 °C

TABLE 2: Summary of extrusion foaming blends, compatibiliser and blowing agent content.

Trial	Material	PE-g-MAH Content (wt %)	Sodium Bicarbonate (pph)
1	NTP	0	0
2	NTP	0	2
3	NTP	0	4
4	NTP: PE-g-MAH: LDPE 50:10:40	10	0
5	NTP: PE-g-MAH: LDPE 50:10:40	10	2
6	NTP: PE-g-MAH: LDPE 50:10:40	10	4
7	LDPE	0	0
8	LDPE	0	2
9	LDPE	0	4
10	NTP: PE-g-MAH: LLDPE 50:10:40	10	0
11	NTP: PE-g-MAH: LLDPE 50:10:40	10	2
12	NTP: PE-g-MAH: LLDPE 50:10:40	10	4
13	LLDPE	0	0
14	LLDPE	0	2
15	LLDPE	0	4

The density and expansion ratio of the material was measured after foaming. Density was determined by measuring a sample block with vernier calipers and weighing the material. The sample mass was then divided by sample volume to obtain sample density (ρ_f) in g/cm³. The expansion ratio (ER) was determined relative to the unfoamed material density (ρ_0). The expected unfoamed density of the given compositions was determined using a weighted average of the density of the individual components. The density for the compatibiliser was assumed to be equal to that of the LLDPE (0.905 g/cm³) and a density of 1.2 g/cm³ was used for NTP.

Cell morphology was observed at low magnification with a Wild M38 optical microscope and at high magnification using a Hitachi S-4700 scanning electron microscope. Samples were first dried at 70°C over 48 hours, then sputter coated with platinum before imaging using an acceleration voltage of 20 kV.

RESULTS AND DISCUSSION

NTP and NTP/PE blends were successfully foamed using extrusion foaming using the BOY35A injection moulder. It was generally observed that expansion ratio increased as the melt temperature increased, with the exception of PE (which was very hard and difficult to cut for analysis), with a processing temperature of 165°C giving the greatest expansion ratio for NTP (4.4). At greater temperatures the material was too fluid to retain the gases and was spitting from the die.

While 165ºC is close to the protein degradation temperature for NTP, processing at just 10-15°C lower (150°C) resulted in little to no expansion. LDPE and LLDPE did not foam without a blowing agent, and blends of NTP with PE showed lower expansion ratios than 100% NTP. NTP blended with LDPE at 165ºC had an expansion ratio of 3 while NTP blended with LLDPE had an expansion ratio of 2.5. Adding 2 pph blowing agent resulted in a finer cell structure but lower expansion ratio for NTP of 3.91, and 4 pph blowing agent gave an expansion ratio of 2.53 and the material looked highly degraded. Adding blowing to the blends also reduced expansion ratios from to 3 to 2.35 for LDPE blends at 4 pph while the expansion ratio did not change for LLDPE and remained at 2.5. Adding blowing agent to LDPE and LLDPE did result in some foaming (**FIGURE 2**), but expansion ratios were unable to be obtained, because the samples were not sufficiently foamed to be able to be cut and measured.

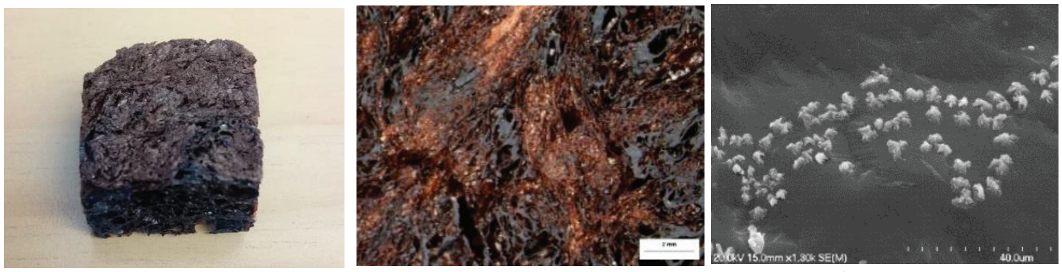
Based on the above observations, NTP can be foamed (**FIGURE 1A)** using the internal moisture content and possibly urea and triethylene glycol, which are likely to flash off with the water. NTP does not need to be blended or have a blowing agent added. Blending NTP with PE required a second extrusion step which reduced the amount of water present for foaming by about 6%. In addition, the amount of water present was lower because the amount of NTP was lower in the blends overall. Adding the blowing agent resulted smaller cells due to increased bubble nucleation, but resulted in lower expansion ratios.

The resulting NTP foam appeared fibrous on a macro scale and the cell morphology was not completely uniform (**FIGURE 1B**). In 100% NTP foams, distinct regions of large and small cells were observed. Thin walls were associated with highly foamed areas with small cells while the larger cells are often surrounded by a region of unfoamed material. The addition of 2 pph blowing agent modified the morphology such that a smaller more uniform cell structure was observed. However, the addition of blowing agent did not result in greater expansion. SEM images of NTP with 2 pph sodium bicarbonate revealed a series of cells which were more defined in their cell boundary, but larger than those small cells observed in NTP alone. The material directly surrounding these cells is clearly devoid of smaller cells and many of the cells are elliptical in shape, most likely due to the direction of material flow during foaming. However at higher magnifications very thin cell walls are visible suggesting that the overall expansion of this material can be improved further.

For pure LDPE, as sodium bicarbonate content increased the number of visible cells also increased, as expected. Their size however remains very similar. A similar trend was observed for LLDPE with blowing agent although there appears to be more cell coalescence occurring, with localized regions of cells with very thin walls for one or two regions of the cell perimeter with the rest surrounded by unfoamed material. Overall, a more cellular structure was observed for LDPE as opposed to LLDPE.

The NTP:PE blends also developed cells which increased in number and decreased in size with increased blowing agent. The cellular structure of these blends is chaotic with a wide distribution of cell sizes in both cases. However, a more defined cellular structure is observed for NTP:LDPE blends as opposed to NTP:LLDPE blends and once again the cells have thinner wall structures. SEM images at higher magnification showed some very thin wall structures which could almost be described as open cell. However the cells appear to be open only on the surface with no fibrous crosslinked structure below (complete walls visible). This is most likely due to cell rupture which occurred when a vacuum was pulled on the sample for SEM analysis.

SEM analysis at high magnification also revealed a possible nucleating agent in embedded in the walls of the cells (**FIGURE 1C**). Elemental analysis of these particles indicated sodium, sulphur and oxygen was present. This is most likely residual sodium sulphite or sodium dodecyl sulphate which did not dissolve fully during mixing. Alternatively sodium sulphate is formed when sodium sulphite oxidizes and sodium sulphate peaks have previously been noted in powder x-ray diffraction and Fourier transform infra-red analysis of NTP.



A B C

FIGURE 1: A. Block of NTP foam **B.** Cell structure by optical microscopy x6.4, **C.** SEM image of particles present in cell wall on which elemental identification was conducted.

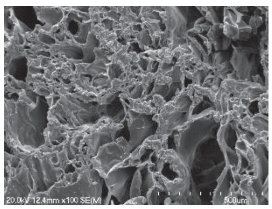
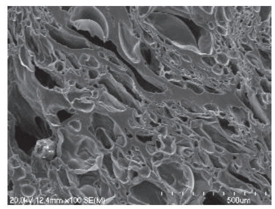
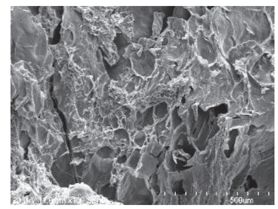
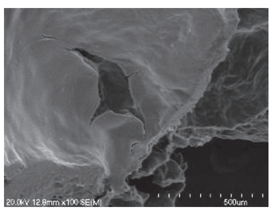
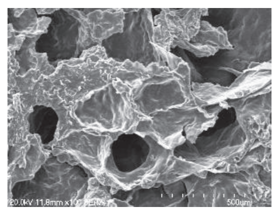
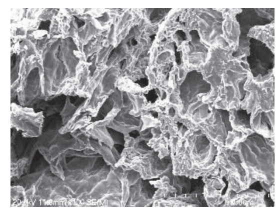
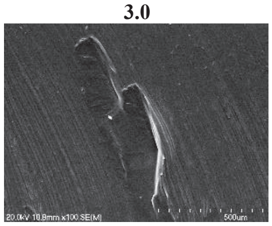
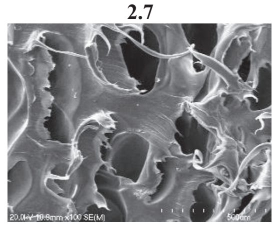
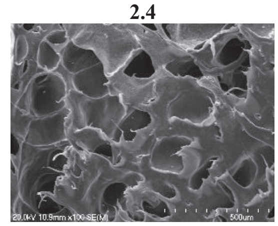
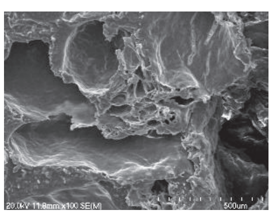
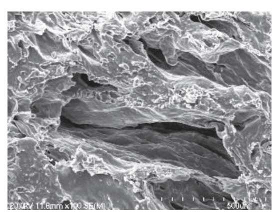
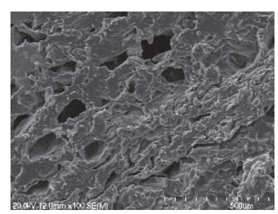
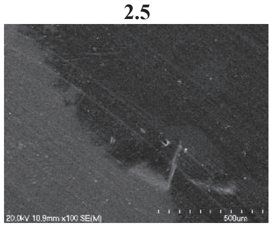
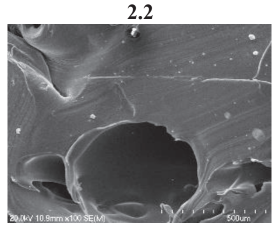
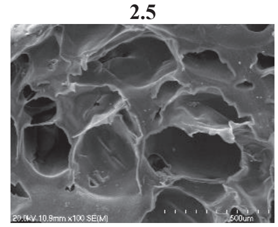
	Blowing Agent Content – Sodium Bicarbonate		
Material/Blend	**0 pph**	**2 pph**	**4 pph**
NTP Crude	 **4.4**	 **3.9**	 **2.4**
50:10:40 LDPE	 **3.0**	 **2.7**	 **2.4**
LDPE ER-N/A			
50:10:40 LLDPE	 **2.5**	 **2.2**	 **2.5**
LLDPE (ER-N/A)			

FIGURE 2: Comparison of observed cellular morphology for foams produced at 165°C. Images are at x150 magnification. Expansion Ratios (ER) are shown below images

An ammonia smell was noticed when foaming NTP and NTP containing blends. Like sodium bicarbonate urea is capable of thermally decomposing to form gaseous reaction products. For sodium bicarbonate water and CO_2 are direct products [7], and although urea can thermally decomposes to ammonia, it is more likely to undergo a hydrolysis reaction due to the presence of water and heat and will produce NH_3 and CO_2 [8]. Likewise, both sodium bicarbonate and urea could potentially react with exposed R groups on the protein chain (carboxylic) to evolve the same gaseous products [8], explaining the ammonia smell observed.

The greatest expansion ratio was observed for 100% NTP, this sample contained no added sodium bicarbonate as a blowing agent and therefore would have resulted in the lowest CO_2 evolution by any mechanism. As sodium bicarbonate content increased in any blend containing NTP the expansion ratio decreased, suggesting that an increased ability to generate CO_2 was not beneficial and may be linked to the ratio of gaseous NH_3 to CO_2 where low CO_2 is favored (if these species are not just a by-product of this method). CO_2 is known to be an excellent blowing agent for PLA in both batch and continuous systems [4], while batch foaming of thermoplastic zein and gelatin determined that N_2 or high N_2/low CO_2 mixtures were preferable for these two proteins [9]. The rapid reduction in pressure at the die may also result in a flashing of water and TEG (dictated by vapour –liquid equilibrium).

Future work will determine which component of the system is the primary blowing agent in the case of NTP and NTP – bicarbonate blends. This will be determined by examining the amount of urea lost from the system, the moisture of the resulting products and the loss of TEG through phase–equilibria and changes in mechanical properties of these foams. The effect of other processing variables such as injection pressure, injection speed, cycle time, shot size and back pressure will also be investigated to further improve the expansion ratio of NTP foams.

CONCLUSIONS

NTP was successfully foamed without blowing agent or blending using a BOY-35A injection moulder, one of the few proteins for which foaming has been successful without blending or rheological modification. The greatest expansion ratio for NTP was 4.4 at 165ºC. Blending with LLDPE and LDPE and adding blowing agent reduced expansion ratios. Foam morphology appeared fibrous with a mixture large and small cells. SEM pictures suggest a possible role of sodium sulphite, sodium dodecyl sulphate or sodium sulphate as a nucleating agent. Future work will investigate the role of internal water, urea, and TEG in NTP foaming.

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