Preparation and Characterisation of Decoloured Novatein® and modified PLA blends

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Abstract

Modified Poly (lactic acid) (PLA) was blended with Decoloured Novatein® (DNTP), a thermoplastic protein material using reactive extrusion to produce a degradable material with improved properties compared to neat Decoloured Novatein®. PLA was modified through free radical grafting of itaconic anhydride to create reactive side-chain groups. Varying ratios of DNTP/ PLA-g-IA or PLA were prepared. Blending DNTP with PLA was found to increase tensile strength between 22% to 538% and modulus between 201 GPa to 3193 GPa, whereas the strain at break decreased between 80% to 94% depending on the blend ratio. The glass transition temperature of the blends which was measured as the tan δ peak, also revealed an increase when compared to neat DNTP. Scanning electron microscope revealed an enhanced interfacial adhesion between the two phases in the blends with PLA-g-IA suggesting a more homogenous microstructure. WAXS result revealed an insignificant decrease in the crystallinity of the blends compared to neat DNTP, indicating that blending with PLA had no structural effect on DNTP. The results show the possibility and feasibility of blending DNTP with PLA for use in agricultural and packaging applications.

1. Introduction

The rise in the cost of petroleum based polymer has led to an increased trend in the replacement of the synthesic polymer with bio-based polymers. PLA, protein, starch and gluten are among the bio-based polymers that are very attractive as replacement due to their availability and properties [1-3]. PLA has experienced substantial growth in its application as a result of its unique properties such as glossy optical appearance, biodegradability, compostability, high tensile strength and good barrier properties toward carbon dioxide, oxygen and water [4-6]. PLA is a biodegradable thermoplastic polyester derived from corn starch, with several

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applications in biomedical and pharmaceutical fields as a material used in surgical operations, tissue regeneration, and drug delivery systems [7]. PLA is also considered suitable for high-volume packaging applications [4, 8] because of its good barrier properties to aromas and permeability to carbon dioxide, oxygen and water vapour compared to synthetic polymers. However, PLA is expensive and has low heat deflection temperature which remains as limitations for wider application. Therefore PLA has often been blended with other polymers to reduce cost and improve blends properties [4, 9-11]

Decoloured Novatein thermoplastic protein (DNTP) is a newly developed biopolymer using bloodmeal as starting material [12, 13]. DNTP is best suited for agricultural and horticultural applications such as weasand clips, weed mat pegs, biodegradable plant pot and seedling trays. DNTP is a protein polymer consisting of complex molecules with strong intra- and intermolecular interactions. These strong interactions make the melt processing of DNTP such as extrusion and injection moulding very difficult unless an adequate amount of plasticizers are added to promote mobility and flexibility of the protein chains enabling flow and consolidation during processing. Low molecular weight polyols such as glycerol, propylene glycol, ethylene glycol and their derivatives [13-17] are used as plasticizers for proteins to reduce intermolecular interactions and glass transition temperature Tg. However, the amount of plasticizer used affects the material's mechanical properties as well as leads to phase separation [5, 9]. Previous research has shown that DNTP can be successfully processed using the extrusion and injection moulder [18]. However, like every other protein polymer, moisture evapourates during processing which leads to a highly brittle material and loss of functionality. Blending DNTP with other polymers can improve its processability and mechanical properties. Researches has shown that blending protein with other hydrophobic thermoplastic is an alternative to increase the processability and moisture resistance of the protein based polymer products. Therefore, DNTP will be blended with PLA. However, the problem with this blend system is the poor interfacial interaction between the hydrophilic DNTP and hydrophobic PLA. Compatibilizer such as poly-2-ethyl-2-oxazoline (PEOX) [9, 19], polymeric methylene diphenyl diisocyanate (pMDI) [5, 20], maleic anhydride [21, 22], methylene diphenyl diisocyanate (MDI) [23, 24] and itaconic anhydride [25] have been used to enhance the interfacial interaction between PLA and other protein polymers.

Research on compatibilized blends of protein thermoplastics and polybutylene succinate reported an improvement in water resistance and tensile strength [5]. Blends of soy protein and PLA was found to increase tensile strength, reduced water absorption of soy plastic and a co-

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continuous phase was observed for soy protein concentrate (SPC) and PLA [9]. Blends of cereal protein and poly (hydroxyl ester ether) without compatibilizer was reported to exhibit acceptable mechanical properties due to the strong hydrogen bonding between the two components [26]. Using a small amount of maleic anhydride (MA) grafted on low-density polyethylene (LLDPE), An improvement in the compatibility between Novatein thermoplastic protein (NTP) was observed as well as improved tensile strength and reduction in water absorption of NTP [20].

Itaconic anhydride (IA) is a highly reactive monomer in free radical grafting as it has the abililty to produce tertiary radicals [27]. Although IA has not been extensively studied but it has been used as a renewable monomer for synthesing bio-based copolymers through conventional copolymerization [28], also can be used for acetylating lysin, tyrosine and cysteine [29]. IA is extremely stable when reacted with proteins compared to MA.

In this study, blends of DNTP and PLA compatibilized with itaconic anhydride were investigated. The main objective of this study was an attempt to demonstrate that DNTP can be used for PLA blends, as other proteins and starch has already been used for PLA blends. It also considered the improvement of processibility and properties of DNTP based plastic through blending with PLA. The morphology, thermal, mechanical and water absorption properties of DNTP/PLA blends were investigated.

2. Experimental

2.1. Materials

Bloodmeal was obtained from Wallace Corporation Limited, New Zealand and used as received. Analytical grade itaconic anhydride (IA), dicumyl peroxide (DCP), acetone, 30 wt % hydrogen peroxide, technical grade sodium dodecyl sulphate (SDS), triethylene glycol (TEG) were purchased from Sigma Aldrich NSW, Australia. Peracetic acid (Peraclean 5) was purchased from Evonik Industries, Morrinsville, New Zealand. Poly(lactic acid) (PLA) grade 3051D was purchased from NatureWorks Ltd in pellet form. Distilled water was produce onsite.

2.2. Sample preparation

2.2.1. Interfacial modification of PLA

PLA was modified through free radical grafting of itaconic anhydride [6] to create reactive side-chain groups. PLA was dried at 80 °C for 4 hours to control moisture. 4.2 parts per hundred

PLA (pph) itaconic anhydride and 0.8 pph dicumyl peroxide were dissolved in 30 mL acetone. The preformed solution was poured over the oven dried PLA and was keep in the fuse hood for about 2 hours. The solution was decanted before oven drying the PLA for 3 hours at $50\,°C$. The modified PLA (PLA-g-IA) was extruded using a LabTech twin screw co-rotating extruder having a screw diameter of 20 mm and L/D of 44:1, at temperature profile of 145 (feed zone), 145, 165, 165, 180, 180,180, 180, 160, 160, 155 $°C$ (die zone). A constant screw speed was maintained at 150 rpm. A vaccum pump was attached on the 7th heating zone of the extruder to get rid of vapour generated during extrusion. To avoid the crystallization of the extruded PLA-g-IA, it was collected in a water bath upon exiting the die and afterwards pelletized. The pelletized PLA-g-IA was oven dried for 12 hours prior to blending with Decoloured Novatein (DNTP) to minimise hydrolysis during melt processing.

2.2.2. Bloodmeal decolouring and Decoloured Novatein preparation

Bloodmeal was decoloured using the standard method with solution of peracetic acid (PAA) [30, 31]. 4 wt% PAA solution was prepared by diluting 5 wt% stock solution with distilled water with a constant percentage ratio of 80:20 respectively. 150 g bloodmeal was decoloured by adding 450 g of 4 wt% PAA in a high speed mixer. The mixture was allowed to mix continuously for 5 min to ensure homogenous decolouring of bloodmeal. 450 g of distilled water was added and mixed for another 5 min to ensure complete dilution of the slurry. The slurry was neutralized by adjusting to pH = 7 with sodium hydroxide solution. The neutralized slurry was filtered using a wire mesh sieve with aperture size 60 and subsequently washed by adding another 450 g of distilled water. The decoloured bloodmeal was dried approximately 15 hours in a 75 $°C$ oven.

Decoloured Novatein (DNTP) was formulated by dissolving 6 part per hundred decoloured bloodmeal (pphD) SDS in 40 pphD water heated to 60 $°C$ while stirring . the solution was added to decoloured bloodmeal powder in a high speed mixer and mixed for 5 min. 30 pphD TEG was added to the mixture and mixed for another 5 min to ensure homogeneous mixture is obtained. The mixed material was stored in an air tight bag overnight in a 2 $°C$ fridge to equilibrate.

2.2.3. Blends preparation

DNTP was formulated prior to blending. Blends containing 30:70, 50:50, 70:30 and 90:10 (w/w) DNTP/PLA-g-IA or PLA were prepared. The performed DNTP and PLA-g-IA or PLA blends were then compounded using a twin screw co-rotating extruder (LabTech). The extruder

barrel had eleven heating zones and the screw speed was maintained at 150 rpm. The compounding extrusion temperature varied from 100 (feed zone) to 180 $^{\circ}$C (die zone) depending on the DNTP content which required a reduction in compounding temperature with an increase in DNTP content as it's formulation contained 40 parts of water that could lead to PLA hydrolysis. The extrudate was granulated using a Tri-blade granulator from Castin Maunfacturing Limited.

2.2.4. Test specimens preparation

ASTM D638-14 Standard tensile test samples [32] and ISO 179-1:2010 impact test samples [33] of the blends were injection moulded using a BOY 35A injection moulding machine. The samples were injected through a cold runner into a 60 $^{\circ}$C water heated mould. The injection moulder has five heating zones including the feed and the die zones. The feed temperature remained constant at 100 $^{\circ}$C, the barrel temperature varied between 100 to 140 and the die temperature varied between 120 to 140 depending on the formulation. The screw speed was constant at 150 rpm. The sample specimens produced were also used for water absorption, thermal and morphology testing.

2.3. Sample Analysis

All samples were conditioned for 7 days at 23 $^{\circ}$C and 50 % relative humidity before testing except otherwise stated.

2.3.1. Mechanical properties

The mechanical testing was performed according to ASTM D638 using Instron Universal Testinf machine (model 33R4204) at a crosshead speed of 5 mm/min and an extensiometer guage length of 50 mm. 10 replicates were tested for each sample type to obtain an average value.

The impact testing bars produced from the injection moulder had diameter of 80 x 10 x 4 mm^3. Charpy edgewise impact strength was performed according to ISO 179-1:2010 using a RAY-RAN Pendulum Impact System. The bars tested were notched according to standard. 10 bars were tested to obtain average impact strength of the material.

2.3.2. Thermal analysis

Dynamic mechanical analysis (DMA) was conducted using Elmer DMA 8000 fitted with a high temperature furnace and cooled with liquid nitrogen. Rectanglar samples (30 x 9 x 4 mm) were cut from injection moulded samples and tested in a single cantilever fixture using free

length of 12.5 mm and scanning temperature from -80 to 150 $^{\circ}$C at 2 $^{\circ}$C/min . data was collected at multiple oscillation frequencies (0.1 – 30 Hz). Tan δ peak values were recorded as glass transition temperatures.

2.3.3. Wide angle X-ray scattering measurement (WAXS)

WAXS was used to measure the XRD pattern of the blends. WAXS was performed with a philips X-ray diffractometer operating at 40 Kv and 40 mA using CuKα radiation. The diffraction data was collected from 2θ values of 4º to 40º with a step size of 0.013º. a fixed 7.5 mm anti-scatter slit, fixed incidence beam mask of 10mm and a soller slit of 0.04 rad were used. *The data collected was baseline corrected from 5-40º and amorphous halo was fitted to this region to determine crystallinity of the blends.*

2.3.4. Fracture morphology

The phase structure of the blends was investigated using Hitachi S-4700 field emission scanning electron microscope (SEM). The injection molded specimens were cryofractured using liquid nitrogen. The specimens were sputter coated with platinum using Hitachi E-1030 Ion sputter before scanning.

3. Results and Discussion
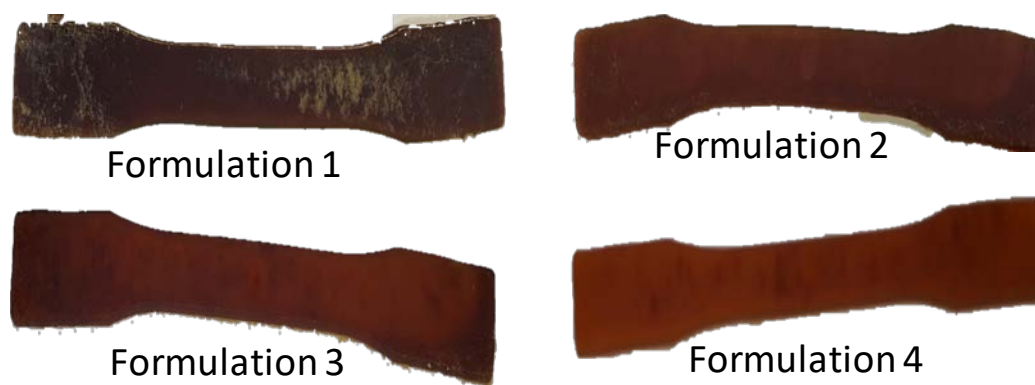
Different formulations of DNTP were prepared based on varying the additives. Water was varied between 30 and 40 pphD, TEG was between 20 and 30 pphD and SDS was between 3 and 6 pphD to produce four sample formulations. The formulations were accessed for blend suitability with PLA based on ease of processing, mechanical and visible colour of produced sample. Formulation 2, 3 and 4 had ease of processing and were easily reproducible compared to formulation 1. They were easy to pull out of the mould and most were self-ejected. They showed reduced injection time and barrel refill time compared to formulation 1, which was

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faced with spur and mould blockage. Comparing the visible clarity of samples, formulation 2, 3 and 4 were more transparent. Compromising tensile strength , formulation 2, 3 and 4 showed low modulus, impact strength and strain at break greater when compared. Similar mechanical properties have been reported for bioplastic produced from decoloured bloodmeal [13].
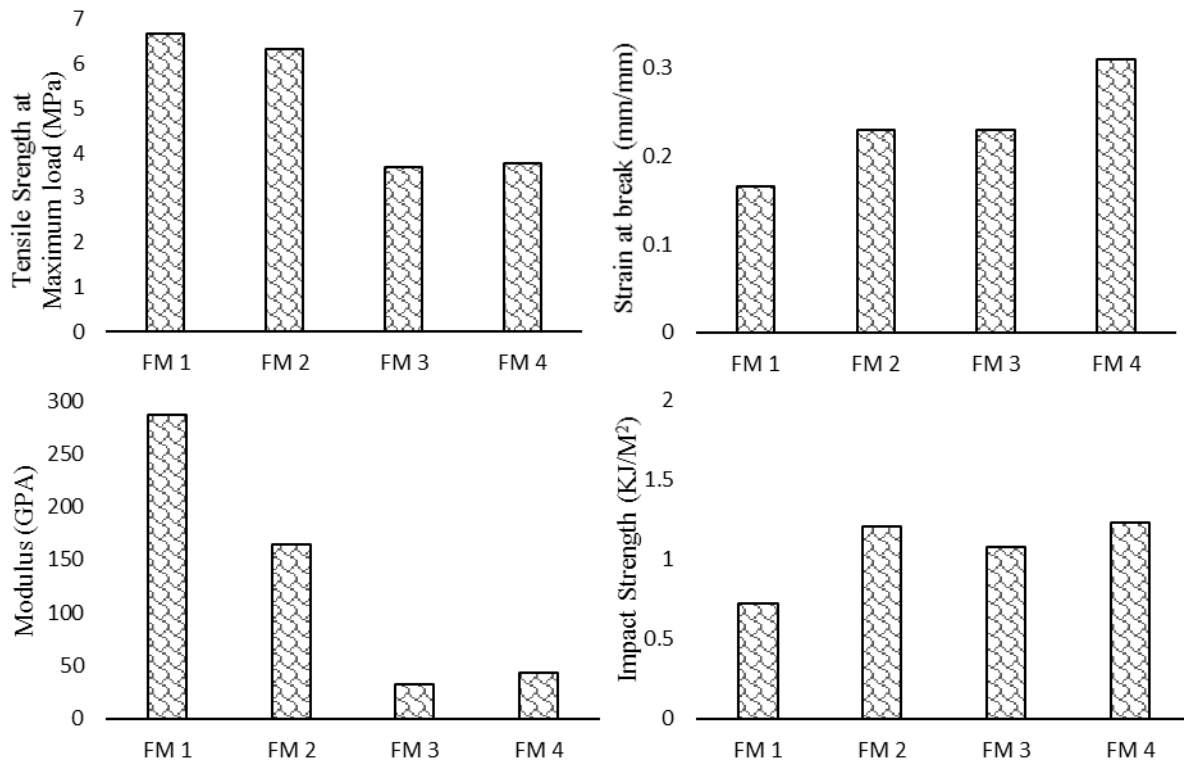

Figure 1: Mechanical properties of DNTP formulation with different ratio amount additives.

Flexibility, toughness and enlongation are very important when considering a material for sheet production as they describe the material's ductility and are useful in the prediction of material performance during handling and storage. Therefore, formulation 4 was chosen to be investigated further as blends with PLA because it produced better extrudate, injection mouldable and brighter samples, having better strain at break, low modulus and good impact strength.

3.1 Blending and processing

Two different blend approaches were used to determine the best approach for DNTP/PLA-g-IA or PLA blends. In the first variation, PLA-g-IA or PLA was blended with pre-extruded

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granules of DNTP and the second variation was to blend PLA-g-IA or PLA with DNTP powder.

3.1.1. Extrusion processing of the blended material

Extruding the blends of DNTP/PLA-g-IA or PLA produced either consolidated or semi-consolidated extrudate with semi or reasonably smooth surface. Extrudate flowed out of the extruder with moderate torque and pressure. The produced extrudate was flexible and rubbery prior to cooling. Small surface defects such as cracks and shark skinning were observed with the blends with high ratio of DNTP. The produced extrudate were granulated and injection moulded.

3.1.2. Injection moulding of the blended material

Injection moulding of blended DNTP granules and PLA-g-IA or PLA

The blends with pre-granulated DNTP could not be injection moulded due to excessive blockage of the injection moulder barrel and protein degradation. Adding of Struktol processing aid had no effect on the blend processing as it became more difficult to feed through the barrel. This was considered an effect of lack of plasticizer in the blend, which might be as a result of excess heat run on DNTP resulting to loss of plasticizers, considering that moisture was also controlled to avoid the hydrolysis of PLA. Therefore an approach to reduce DNTP heat run during processing was considered leading to blends of DNTP powder and PLA-g-IA or PLA.

Injection moulding of blended DNTP powder and PLA-g-IA or PLA

The injection moulding of DNTP powder and PLA-g-IA or PLA worked well without processing aid and produced flexible and consolidated sample bars. The injection of blends produced three type of sample bars as shown in Table 1.

Table 1: description of injection processing of blends

Injection type	Description
1	not self ejected out of the mould, longer injection time and barrel refill time, very difficult to pull out of the mould due to spur block.
2	not self injected out of the mould, reduced injection time and barrel refill time, easy to pull out of the mould unit and spur section.

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| 3 | mostly self injected out of the mould and easy to remove from the mould unit manually, reduced injection time and barrel filling time. |

Injection type 1 was observed mainly for blend having high amount of PLA while for blends having lower amount of PLA injection type 2 and 3 were observed and injection type 3 was observed for 50:50 blends. Blending PLA and DNTP powder was injection mouldable and showed ease of processing, therefore the second variation was chosen to be the optimal method for processing DNTP/PLA blends. The properties of the sample produced were investigated.

3.2 Phase morphology

The study of polymer blend morphology is important as it is related to the mechanical and barrier properties of the blend [14, 34] and it is essential in understanding property-structure relationship of the material. Most polymer blends are immiscible therefore produce a heterogeneous morphology [34]. Compatibilizers are used to reduce the interfacial tension in polymer blends thereby stabilizing the morphology, often resulting in a co-continuous structure [5]. Co-continuous morphology exhibits a combination of both polymer components characteristics [35], this is formed mainly around the point of phase inversions such that the matrix is undistingishable from the dispersed phase.

Figure 2 shows the cryofractured phase structure of DNTP/PLA and DNTP/PLA-g-IA blends with DNTP/ PLA-g-IA or PLA ratio varying between 30:70 to 90:10 (w/w). A dispersed phase morphology was observed with blends without itaconic anhydride showing one phase which is rich in DNTP and another that is rich in PLA (Figure 2.c, d, e). Also, the interstices between the DNTP phase and PLA matrix were clearly observed for the uncompatibilized blend indicating poor interfacial adhesion. This is expected, as DNTP contains 90% protein which is highly polar and hydrophilic while PLA is hydrophobic therefore will lead to poor interfacial interaction between the two phase. Blend of Novatein and polybutylene succinate (PBS) without compatibilizer was reported to have poor interfacial adhesion [5]. As DNTP content increased, the diameter of DNTP rich phase increased for blends without IA. This is attributed to the poor interfacial adhesion between DNTP and PLA phase. However, the addition of IA (Figure 2. c', d', e') showed an improved even dispersion of DNTP within the matrix. Even at high DNTP content (Figure 2. e'), a virtually undistinghable DNTP phase was observed. Although some interstices were still observed in the compatibilized sample but they are fewer and smaller compared to the uncompatiblized blends.

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The improved dispersion observed with blends compatibilized with IA arose from the formation of branched and crosslinked macromolecules initiated by the reaction of the anhydride group of PLA-g-IA with the amino groups of DNTP. Same phenomena had been reported for compatibilized PLA blends with protein and starch [10, 22]. It has been reported that addition of PEOX improved the interfacial adhesions between SPC/PLA blends resulting to finer structure and homogeneous phase structure [9]

Compatibilization showed no clear effect on 30:70 blend ratio (Figure 2. b and b'), this is believed to be due to the overwhelming effect of high PLA content in the matrix. This was further explored using thermal analysis and wide angle X-ray scattering (WAXS).
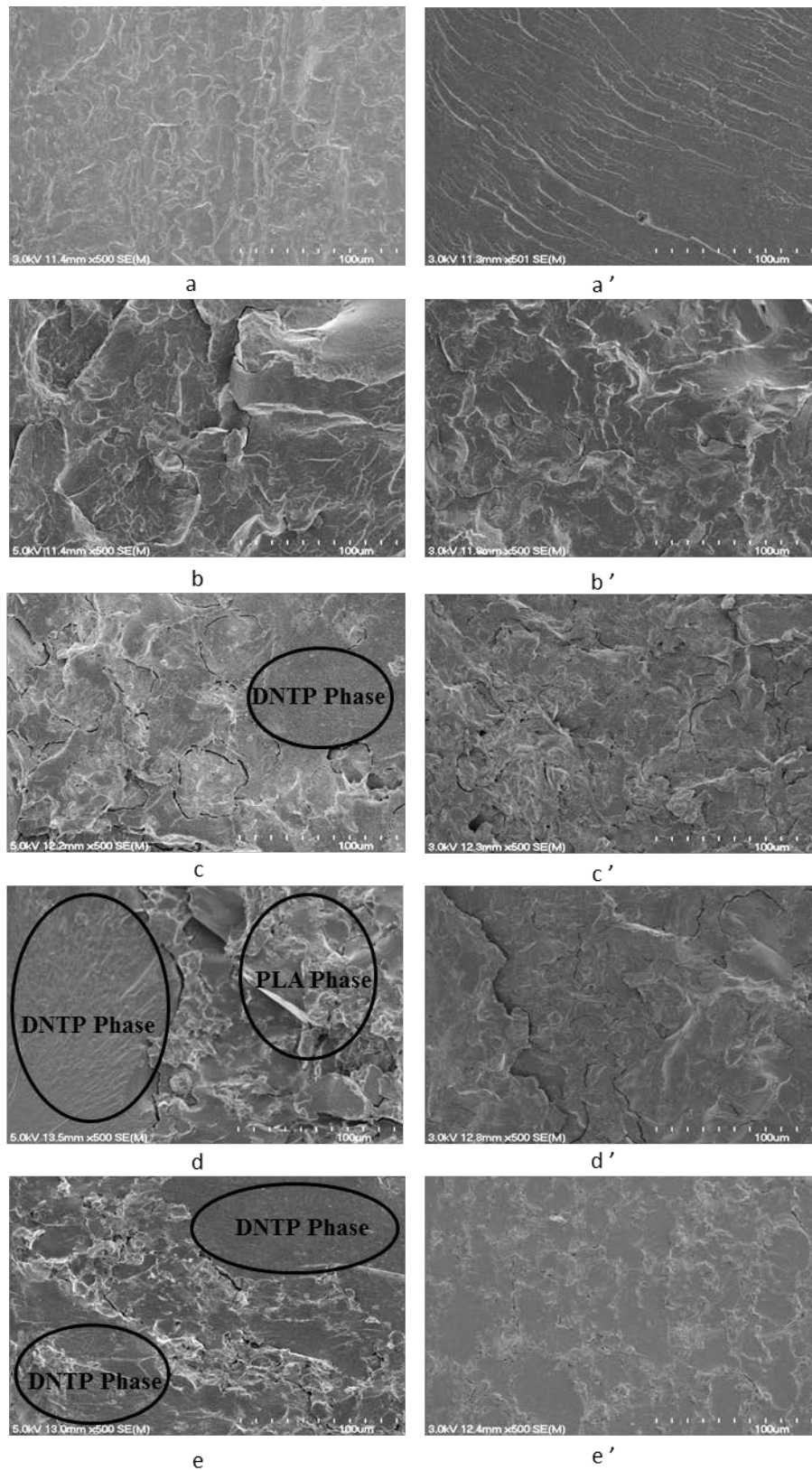
Figure 2: SEM micrographs of cryo-fractured surface of DNTP/ PLA-g-IA or PLA blends. a and a':
PLA and DNTP; b and b': 3070DP and 3070DgP; c and c': 5050DP and 5050DgP; d and d': 7030DP
and 7030DgP; e and e': 9010DP and 9010DgP

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3.3. Dynamic mechanical properties

Understanding thermal transition of a polymer material is very important in the prediction of the material's performace under different end use conditions. DMA have been commonly used to study the molecular relaxation processes in polymers [14] and to determine inherent flow and mechanical properties such as modulus and damping of viscoelastic material over a spectrum of time (frequency) and temperature [36]. Figure 3 show the tan δ and storage modulus (E') of neat PLA, PLA-g-IA and DNTP. PLA and DNTP showed broad and low damping peaks (Tg) while PLA-g-IA exhibited a sharp and high damping peak. The high damping peaks is suggested to be due to PLA-g-IA low crystallinity which makes it very soft when the temperature is above its α-transition. Similar observation have been reported for PLA grade used for blends with soy protein composites [9, 22].
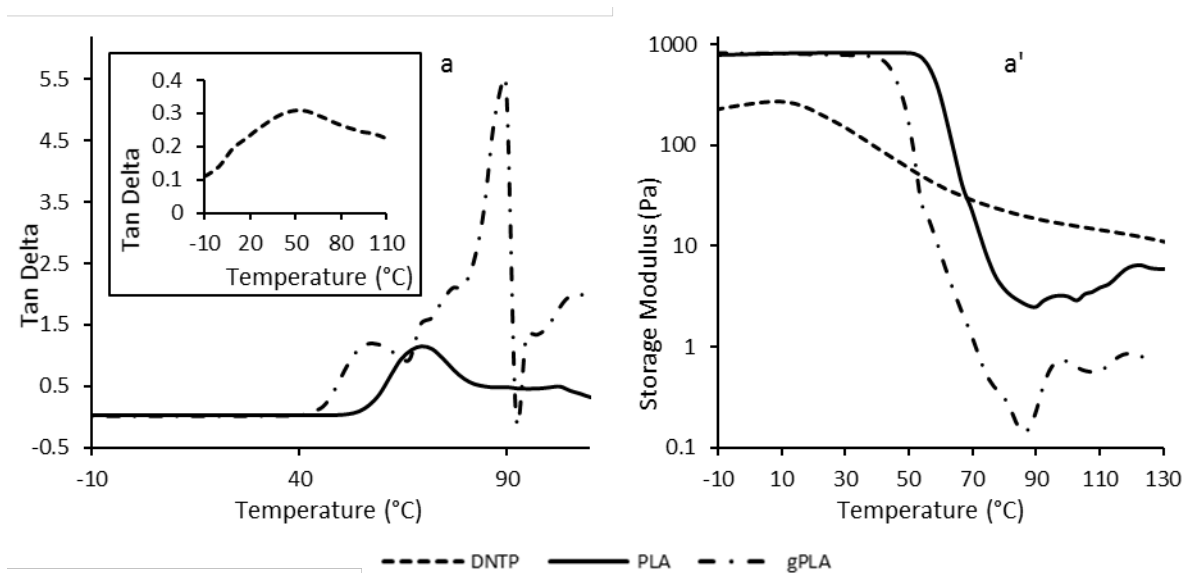

Figure 3: Tan δ and storage modulus (E') of neat PLA, PLA-g-IA and DNTP

The damping peak of PLA and PLA-g-IA in the blends were observed to be lower than that of the neat PLA and PLA-g-IA alone. This suggests that the DNTP component was still in glassy state in the α-transition range of PLA and PLA-g-IA. The compatibilized blends (Figure 4. a') show broader peaks compared to the uncompatibilized blends (Figure 4. a), which suggested that the blends had improved interactions between PLA and DNTP. The damping peak height decreased with increasing DNTP ratio, this is probably attributed to the effective contribution of the DNTP phase to the storage modulus in the rubbery region of PLA [9, 22, 37]. The decrease in Tg observed with the blends is thought to be due to the migration of small molecules of plasticisers from DNTP phase to the PLA matrix during compounding. No significant

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difference was observed in the Tg of the compatibilizer and the uncompatibilizer blends therefore it suggests that compatibilization has no significant influence on the melting point of PLA in the blends.
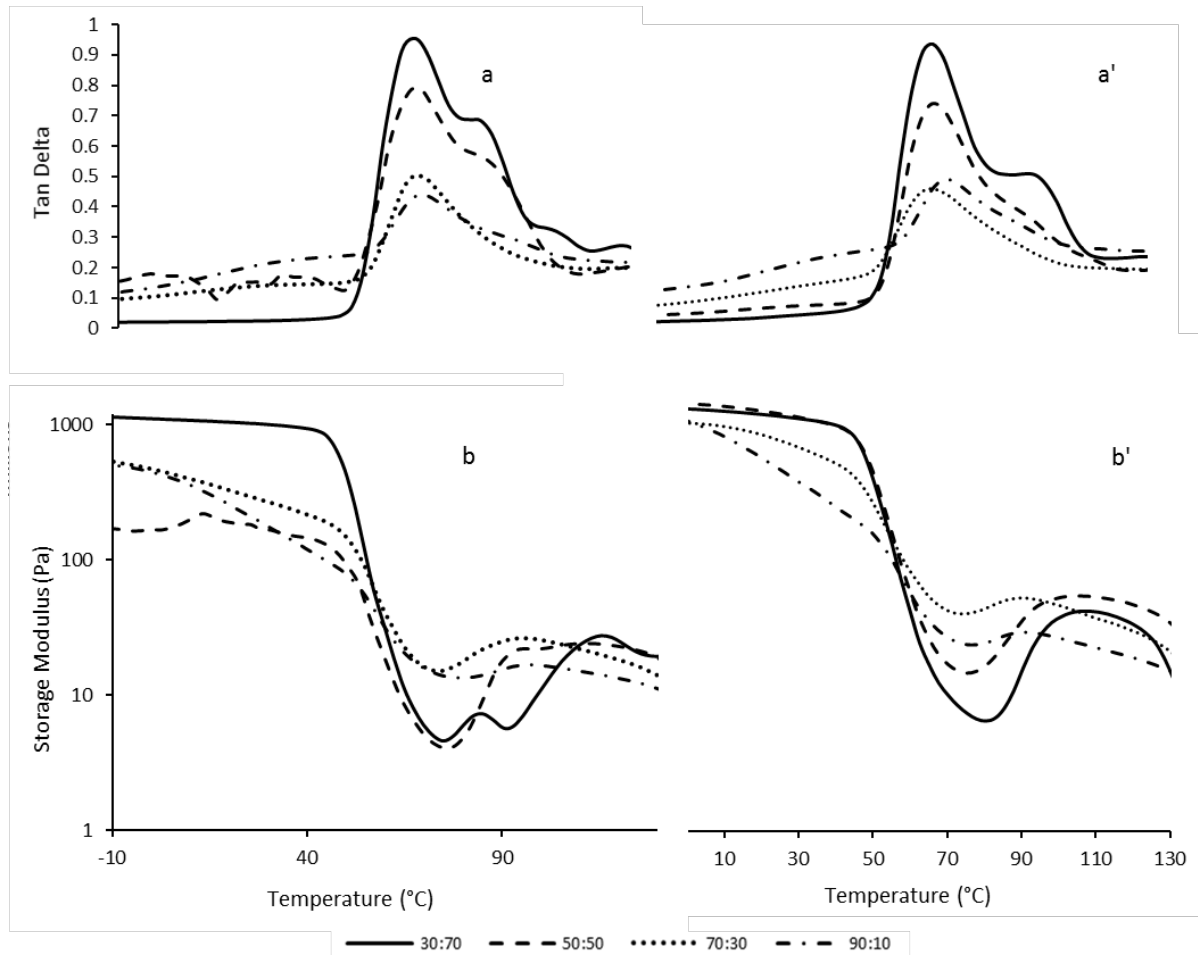

Figure 4: Tan δ and storage modulus (E') of blends. a and b: DNTP/ PLA, a'and b': DNTP/ PLA-g-IA

Two transitions (peak and a shoulder) was observed for the 30:70 and 50:50 blends (Figure 4. a). the first peak correspounds to the α-transition of PLA region and the second peak could be associated with the α-transition of the DNTP region in the blends. 30:70 and 50:50 blends with PLA-g-IA (Figure 4. a') showed a shift in the α-transition of DNTP region towards a lower temperature while the PLA region showed a slight change with compatibilization. This change is suggested to be due to the improved compatibility between both regions or as a result of miscibility of DNTP and the compatibilizer. Jinwen Zhang et al observed same trend with soy protein isolate/PLA compatibilizer with PEOX [9]. At higher content of DNTP, only a single peak was observed and no shift in peak temperature was observed. The storage modulus of the uncompatibilized blends dropped when the Tg of DNTP (≈ 60 ℃) was reached, and then

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recovered to a significant degree between 90 and 95 ºC due to the cold crystallization of PLA. However, this recovery was not observed with the compatibilized blends. The compatibilized blends showed a lower storage modulus than both DNTP and PLA (Figure 3. a') at temperature below α-transition of PLA region. This might be associated with the compatibilization effect of IA on DNTP in the blends making DNTP more flexible in the blends. Ning Wang et al suggested that the addition of maleic anhydride improved the plasticization of starch in starch/PLA blends [10].

3.4. Wide angle X-ray scattering (WAXS) measurement

X-ray diffraction (XRD) is a technique used to measure the atomic arrangement of a material. The XRD data of polymers can be used to study the material's phase change. The WAXS of neat PLA, DNTP and DNTP/PLA blends with and without compatibilizer are shown in Figure 5. An amorphous peak at 16º 2θ was observed for PLA without a crystal and long-range order. PLA-g-IA clearly presents crystalline peaks at 2θ = 16º and 22º. The 2θ at 16º was recognized as (110)/(200) reflection of α-form homo-crystal structure and 2θ at 22º was recognized as (100)/(-120)/(-210) of stereo-complex crystals [38-40]. DNTP is semi-crystalline with less aggregated β-sheet and high number of disordered structure [13]. The peak at 2θ = 9º corresponds to helical spacing and inter- β-sheet and the peak at 2θ = 22º corresponds to repeated distance within each structure.
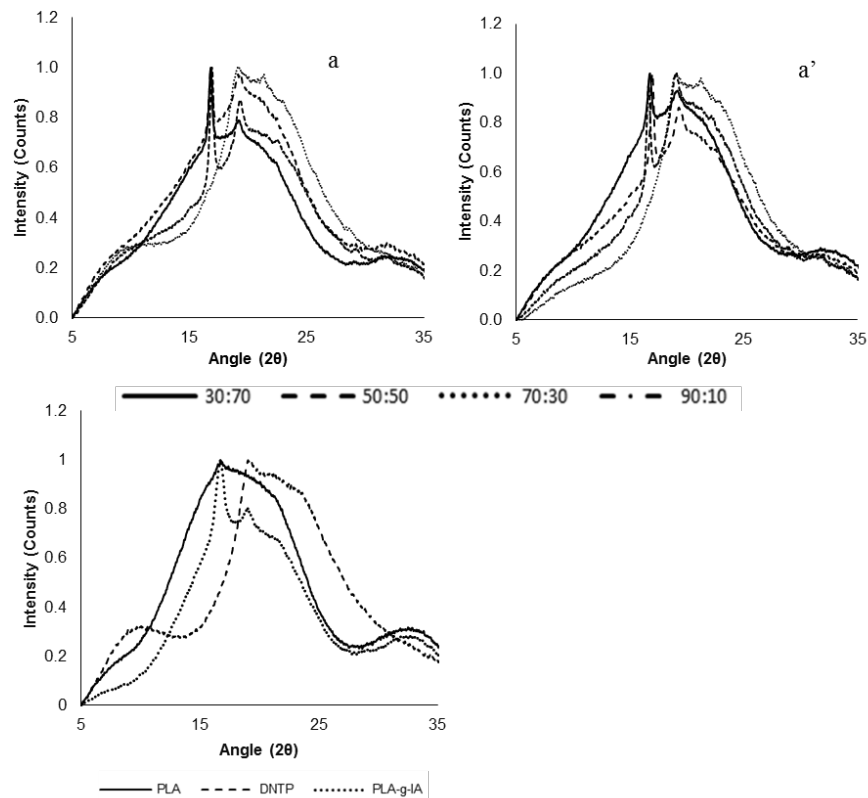
Figure 5: WAXS diffractograms of PLA, DNTP, PLA-g-MA and DNTP/PLA blends without (a) and with compatibilizer (a')

The summation of DNTP and PLA diffractogram looks exactly like the diffractogram of DNTP/PLA blends of both with and without compatibilizer. This suggests the existance of three phases in the blends, the amorphous DNTP, amorphous PLA and crystalline PLA. The compatibilized blends showed a slight reduction in the amorphous region suggesting an intergration of both PLA and DNTP amorphous region. This is probably due to the reduction in DNTP aggromerate observed with SEM thermogram (Figure 2).

No change was observed in 2θ for the two peak at 16º and 22º with the addition of compatibilizer. This suggests that Itaconic ahydride had no compatibilizing effect with the crystal region of the blend therefore may not be a good compatibilizer for DNTP/PLA blends or the degree of PLA grafting is not sufficient to compatibilize DNTP/PLA blends.

3.5 Mechanical properties

Mechanical testing provides valuable information on material's flexibility, toughness and elongation which is useful in the prediction of its performance during processing, handling, storage and final product performance. The mechanical peoperties of PLA, DNTP and DNTP/PLA blends are shown in Figure 6. PLA has been reported to have high tensile strength, impact strength, modulus and low elongation [41] while DNTP has low tensile strength, impact strength, modulus and high elongation [18]. Mechanical properties might be used to assess polymer blends miscibility as it depends on the intermolecular interaction chain stiffiness and molecular symmetry of the individual polymer in the blend matrix [42]. Willemse et al. suggested that tensile modulus of polymer blends depends strongly on the composition and morphology of the blends [43].

Both DNTP/PLA blends with and without compatibilizer showed rigid and brittle behaviour. The modulus of the blends was higher than that of neat DNTP due to the incorporation of rigid PLA.
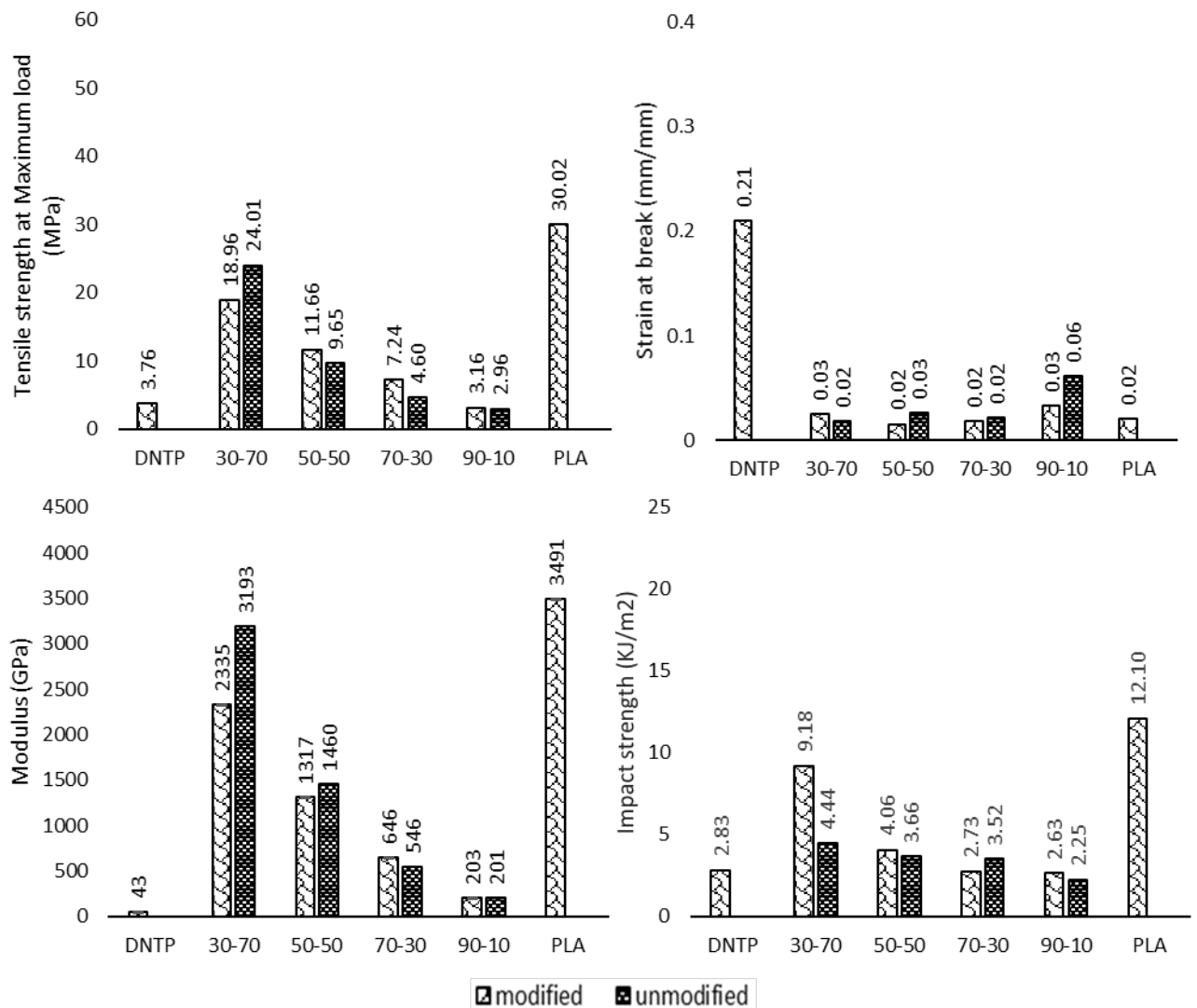
Figure 6: Mechanical properties of DNTP, PLA and DNTP/PLA blends with and without compatibilizer

Tensile strength observed for DNTP/PLA blends were inferior compare to neat PLA. This is as a result of weak interfacial adhesion between the two phases even with the addition of compatibilizer. Previous researches have reported inferior tensile strength for blends of PLA/Novatein [25] and PLA/soy protein [22]. However, all blends showed an improvement in tensile strength compared to DNTP. Further improvement was observed for 50-50 and 70-30 blends with the addition of itaconic anhydride. The mechanical properties of 30-70 compatibilized blends were very poor compared to the uncompatibilized blends while 90-10 blend showed no significant effect. It is assumed that below 50% and above 70% DNTP cotent, DNTP overwhelm the compatibiling effect of itaconic anhydride resulting in poor tensile strength.

The anhydride groups of Itaconic anhydride were likely to react with the amino groups of DNTP protein therefore enhancing the interfacial adhesion as observed with the SEM

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micrographs (Figure 2) which played a role in reducing the size of DNTP phase in the compatibilzed blends. However, this interfacial adhesion is considered to be very weak therefore wasn't strong enough to effect significant improvement in the mechanical properties. This is thought to be probably due to insufficient amount of compatibilizer (i.e. low degree of grafting) or an indication that Itaconic anhydride is not a suitable compatibilizer for DNTP/PLA blends. Rui Zhu et al, reported an increase in both tensile strength and elongation of PLA/Soy protein composite with an increase in compatibilizer content [22].

4. Conclusion

DNTP/PLA blends were successfully prepared by extrusion mixing. The processibility and flowability of DNTP increased after blending with PLA and it was injection mouldable without processing aids. The DNTP/PLA blends showed a co-continuous phase morphology with a wide range of compositions. Blends of DNTP/PLA compatibilized with itaconic anhydride led to significant change in morphology improving the interfacial adhesion between the blended material phases. however, the adhesion between the phases was not strong enough to improve mechanical properties. DMA results, WAXS diffractograms and mechanical properties indicated compatibility of PLA with DNTP and the possiblilty of improving their interfacial interactions. Itaconic anhydride can be used as compatibilizer for DNTP/PLA blends, leading to improved mixing of the two phases. However, the two transition observed in the blend's DMA (although the second transition shifted to lower temperature for 30:70 and 50:50 blends ratio) suggests that the amount of IA in PLA-g-IA is probably not sufficient enough to effect a significant improvement in the blend's mechanical properties. All blends showed low elongation at break and high brittle behaviour thereby creating room for material plasticization and toughening in future investigations. Investigation of DNTP formulation and plasticization will be necessary to optimize process and material's properties.

5. References

1.   Sue, H.-J., S. Wang, and J.-L. Jane, *Morphology and mechanical behaviour of engineering soy plastics.* Polymer, 1997. **38**(20): p. 5035-5040.
2.   Vaidya, U.R. and M. Bhattacharya, *Properties of blends of starch and synthetic polymers containing anhydride groups.* Journal of applied polymer science, 1994. **52**(5): p. 617-628.
3.   Mohamed, A.A., et al., *Thermal characteristics of polylactic acid/wheat gluten blends.* Journal of food quality, 2006. **29**(3): p. 266-281.
4.   Huneault, M.A. and H. Li, *Morphology and properties of compatibilized polylactide/thermoplastic starch blends.* Polymer, 2007. **48**(1): p. 270-280.
5.   Ku-Marsilla, K. and C. Verbeek, *Compatibilization of Protein Thermoplastics and Polybutylene Succinate Blends.* Macromolecular Materials and Engineering, 2015. **300**(2): p. 161-171.

6.   Marsilla, K.K. and C. Verbeek, *Modification of poly (lactic acid) using itaconic anhydride by reactive extrusion.* European Polymer Journal, 2015. **67**: p. 213-223.

7.   Gorrasi, G. and R. Pantani, *Effect of PLA grades and morphologies on hydrolytic degradation at composting temperature: assessment of structural modification and kinetic parameters.* Polymer degradation and stability, 2013. **98**(5): p. 1006-1014.

8.   Auras, R., B. Harte, and S. Selke, *An overview of polylactides as packaging materials.* Macromolecular bioscience, 2004. **4**(9): p. 835-864.

9.   Zhang, J., et al., *Morphology and properties of soy protein and polylactide blends.* Biomacromolecules, 2006. **7**(5): p. 1551-1561.

10.   Wang, N., J. Yu, and X. Ma, *Preparation and characterization of thermoplastic starch/PLA blends by one-step reactive extrusion.* Polymer International, 2007. **56**(11): p. 1440-1447.

11.   Suyatma, N.E., et al., *Mechanical and barrier properties of biodegradable films made from chitosan and poly (lactic acid) blends.* Journal of Polymers and the Environment, 2004. **12**(1): p. 1-6.

12.   Verbeek, C.J.R., M.C. Lay, and A.W.K. Low, *Methods of manufacturing plastic materials from decolorized blood protein*. 2013, Google Patents.

13.   Low, A., *Decoloured bloodmeal based bioplastic*. 2012, University of Waikato.

14.   Hernandez-Izquierdo, V. and J. Krochta, *Thermoplastic processing of proteins for film formation—a review.* Journal of food science, 2008. **73**(2).

15.   Gennadios, A., *Protein-based films and coatings*. 2002: CRC Press.

16.   Zhang, J., P. Mungara, and J.-l. Jane, *Mechanical and thermal properties of extruded soy protein sheets.* Polymer, 2001. **42**(6): p. 2569-2578.

17.   Pickering, K.L., et al., *Plastics material*. 2012, Google Patents.

18.   Verbeek, C.J.R., et al., *Processability and mechanical properties of bioplastics produced from decoloured bloodmeal.* Advances in Polymer Technology, 2017.

19.   Smith, M.J. and C.J. Verbeek, *The relationship between morphology development and mechanical properties in thermoplastic protein blends.* Advances in Polymer Technology, 2017.

20.   Marsilla, K. and C.J.R. Verbeek, *Properties of Bloodmeal/Linear Low-density Polyethylene Blends Compatibilized with Maleic Anhydride Grafted Polyethylene.* Journal of Applied Polymer Science, 2013. **130**(3): p. 1890-1897.

21.   John, J. and M. Bhattacharya, *Properties of reactively blended soy protein and modified polyesters.* Polymer international, 1999. **48**(11): p. 1165-1172.

22.   Zhu, R., H. Liu, and J. Zhang, *Compatibilizing effects of maleated poly (lactic acid)(PLA) on properties of PLA/Soy protein composites.* Industrial & Engineering Chemistry Research, 2012. **51**(22): p. 7786-7792.

23.   Zhong, Z. and X.S. Sun, *Properties of soy protein isolate/polycaprolactone blends compatibilized by methylene diphenyl diisocyanate.* Polymer, 2001. **42**(16): p. 6961-6969.

24.   Huang, J., et al., *Soy protein isolate/kraft lignin composites compatibilized with methylene diphenyl diisocyanate.* Journal of applied polymer science, 2004. **93**(2): p. 624-629.

25.   Walallavita, A., C.J. Verbeek, and M. Lay. *Blending Novatein® thermoplastic protein with PLA for carbon dioxide assisted batch foaming*. in *AIP Conference Proceedings*. 2016. AIP Publishing.

26.   Wang, C., C. Carriere, and J. Willett, *Processing, mechanical properties, and fracture behavior of cereal protein/poly (hydroxyl ester ether) blends.* Journal of Polymer Science Part B: Polymer Physics, 2002. **40**(19): p. 2324-2332.

27.   Sharabasht, M.M. and R.L. Guile, *Copolymerization Parameters of Itaconic Anhydride in Free-Radical Polymerization.* Journal of Macromolecular Science: Part A-Chemistry, 1976. **10**(6): p. 1039-1054.

28. Okuda, T., et al., *Renewable biobased polymeric materials: facile synthesis of itaconic anhydride-based copolymers with poly (L-lactic acid) grafts.* Macromolecules, 2012. **45**(10): p. 4166-4174.

29. Fischer, L. and F. Peissker, *A covalent two-step immobilization technique using itaconic anhydride.* Applied microbiology and biotechnology, 1998. **49**(2): p. 129-135.

30. Low, A., C.J.R. Verbeek, and M.C. Lay, *Treating Bloodmeal with Peracetic Acid to Produce a Bioplastic Feedstock.* Macromolecular Materials and Engineering, 2014. **299**(1): p. 75-84.

31. Hicks, T.M., et al., *The role of peracetic acid in bloodmeal decoloring.* Journal of the American Oil Chemists' Society, 2013. **90**(10): p. 1577-1587.

32. Properties, A.S.D.o.M. *Standard test method for tensile properties of plastics*. 1996. American Society for Testing and Materials.

33. ISO, E., *179-1 (2010).".* Plastics. Determination of Charpy impact properties. Part. **1**.

34. Willemse, R., et al., *Co-continuous morphologies in polymer blends: a new model.* Polymer, 1998. **39**(24): p. 5879-5887.

35. Xie, H.-Q., J. Xu, and S. Zhou, *Polymer blends with two kinds of elastomeric ionomers.* Polymer, 1991. **32**(1): p. 95-102.

36. Menczel, J.D. and R.B. Prime, *Thermal analysis of polymers: fundamentals and applications*. 2014: John Wiley & Sons.

37. Sumita, M., et al., *Dynamic mechanical properties of polypropylene composites filled with ultrafine particles.* Journal of applied polymer science, 1984. **29**(5): p. 1523-1530.

38. Furuhashi, Y., Y. Kimura, and H. Yamane, *Higher order structural analysis of stereocomplex-type poly (lactic acid) melt-spun fibers.* Journal of Polymer Science Part B: Polymer Physics, 2007. **45**(2): p. 218-228.

39. Tsuji, H., H. Takai, and S.K. Saha, *Isothermal and non-isothermal crystallization behavior of poly (l-lactic acid): effects of stereocomplex as nucleating agent.* Polymer, 2006. **47**(11): p. 3826-3837.

40. Mittal, V., et al., *PLA, TPS and PCL binary and ternary blends: structural characterization and time-dependent morphological changes.* Colloid and Polymer Science, 2015. **293**(2): p. 573-585.

41. Martin, O. and L. Averous, *Poly (lactic acid): plasticization and properties of biodegradable multiphase systems.* Polymer, 2001. **42**(14): p. 6209-6219.

42. Joseph, S. and S. Thomas, *Modeling of tensile moduli in polystyrene/polybutadiene blends.* Journal of Polymer Science Part B: Polymer Physics, 2002. **40**(8): p. 755-764.

43. Willemse, R., et al., *Tensile moduli of co-continuous polymer blends.* Polymer, 1999. **40**(24): p. 6645-6650.

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