

# BLENDS OF LINEAR-LOW-DENSITY POLYETHYLENE AND THERMOPLASTIC BLOODMEAL USING MALEIC ANHYDRIDE GRAFTED POLYETHYLENE AS COMPATIBILIZER

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## ABSTRACT

Linear Low-Density Polyethylene (LLDPE) was blended with Novatein Thermoplastic from bloodmeal (NTP.) The compatibilizing effect of maleic anhydride grafted polyethylene (PE-g-MAH) on mechanical, morphology thermal properties and water absorption were studied and compared with blends without compatibilizer. The amount of polyethylene added was varied between 20% to 70% with 10% of compatibilizer. An improvement in compatibility between NTP and LLDPE was evident across the entire composition range only when using compatibilizer. The tensile strength of blends decreased over that pure LLDPE, but never dropped below that of pure NTP. Results showed that blending NTP with LLDPE decreased water absorption significantly, even more so using a compatibilizer. The result is a more water stable material.

## INTRODUCTION

In recent times, biodegradable materials have been studied extensively with increasing interest in the potential of new materials for application in the agriculture, food and electronic industry. The global biodegradable plastics market is expected to grow from 664 thousand metric tons in 2010 to 2330 thousand metric tons in 2016 (MarketsandMarkets, 2001). Amongst all market segments, the starch-based plastic market has the largest share in volume, while PLA-based plastic lead the market in terms of revenue. These markets are expected to continue growing, driving demand for sustainable, eco-friendly biodegradable plastics in the coming decade.

Linear low-density polyethylene (LLDPE) is among the most popular polyethylene products with significant numbers of short branches, commonly made by copolymerization of ethylene with longer-chain olefins. One strategy of improving LLDPE's degradability is to blend it with biodegradable thermoplastics. After disintegration of the biodegradable part by microorganism in the disposal environment, the remaining inert components will slowly decompose and disappear as long as the particle size of the thermoplastic resin is fine enough (Janssen, 2009, Utracki, 1998). Mechanical, physical and thermal properties of blends containing 39.9% starch and LLDPE were similar to those pure LDPE indicating suitability for all industrial applications with the advantages of improved biodegradability. (Vieyra Ruiz et al., 2010).

Plants have been used to produce plastics for some time, with plastics made from corn, starch and peanuts as well as soy protein. However, in the research of sustainable materials from non-potential food sources, bloodmeal is one of the best candidates for bioplastic manufacture. Raw blood is commonly dried into an insoluble powder with at

least 85 wt% proteins and less than 10% moisture, called bloodmeal. The first stage of developing Novatein thermoplastic(NTP) from bloodmeal showed that dry processing techniques, such as extrusion and injection moulding were successfully used to produce a bioplastic with good mechanical properties (Verbeek and van den Berg, 2010a, Verbeek and van den Berg, 2010b, Verbeek and van den Berg, 2011). However, most blends involving natural and synthetic polymer are immiscible due to the absence of specific interactions thus requiring a compatibilizer to achieve miscibility.

Maleic anhydride is one of the popular choices used as monomer to graft onto polypropylene, polyethylene, and various other polymers (Sathe et al., 1994, Vermeesch and Groeninckx, 1994, Gaylord and Mehta, 1982). PE and ethylene vinyl acetate(EVA) having maleic anhydride functional group that interact with hydroxyl group in starch has been studied and the samples displayed excellent physical properties although there was reduction in elongation of the blends (Ramkumar et al., 1996). References are available in which maleic anhydride is used as monomer to graft various other polymers (Carlson et al., 1999, Mani et al., 2000, Bhattacharya et al., 1995, Pesetskii et al., 2002, Slavovs et al., 2005, Mani et al., 1999). The purpose of this study was to blend NTP with low linear density polyethylene (LLDPE) containing PE-g-MAH as compatibilizer. The effects of PE-g-MAH on mechanical and thermal properties, morphology, and water absorption properties were analyzed as a function of composition, between 20 and 70 wt% LLDPE.

## **MATERIALS AND METHODOLOGY**

### **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 sulphate were purchased from BiolabNz and BDH Lab Supplies. Agricultural grade urea was obtained from Balance Agri-nutrients (NZ). LLDPE, Cotene 3901 was purchased from J.R. Courtenay (N.Z.) Ltd.

### **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 in a high speed mixture for 5 minutes. Triethylene glycol (40 g) was added to the mixture and blended for another 3-4 minutes. The mixtures were stored for at least 24 hours prior to extrusion.

### **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.

## **Injection Moulding**

Standard tensile bars (ASTM D638) were prepared using BOY 35 A Injection Moulding Machine with temperature profile of 100,115,130,135,140°C from feed to exit die zone. The specimen were conditioned in conditioning chamber at 23°C and 50% relative humidity, equilibrating to ~ 10% moisture content

## **Mechanical Testing**

Tensile specimens were tested on an 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 Young's modulus were analysed for conditioned samples.

## **Morphology**

The microstructure of BM/LLDPE was investigated with scanning electron microscopy (SEM) Hitachi S-4700. Samples were immersed in liquid nitrogen and the fracture surfaces were sputter-coated before scanning. An accelerating voltage of 5kV was applied.

## **Water Absorption**

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

## **Dynamic Mechanical Analysis (DMA)**

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

## **Formulation**

Table 1 gives the formulations of all sample studied in this work. NTP was extruded and injection moulded with LLDPE using the same profile as above.

# **RESULTS AND DISCUSSION**

## **Mechanical Properties**

Figure 1 shows the tensile strength of NTP/LLDPE blends with and without compatibilizer. The tensile strength of blends without compatibilizer decreased with increasing NTP contents from 20% - 30%, but increased significantly at 50%. Above 50% it dropped gradually up to 70% NTP. The decrease of tensile strength is 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. The phase morphology is discussed later.

An interesting observation was the increase in tensile strength at 50% NTP; increasing to 8-9MPa. 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. Typically, at low concentration, that polymer would be the dispersed phase. As the concentration is increased, some phase inversion may occur leading to a region where neither polymer is the dispersed phase and is called co-continuous phase (Willemse et al., 1998). It was thought that at almost equal proportions that this type of morphology could have led to the observed increase in strength and was further explored in SEM.

The Young's modulus and elongation at break showed similar behaviour (Fig 2 and 3). A sharp drop in elongation at break was observed at low NTP content. Considering that NTP is much more brittle than LLDPE, 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 (Pedroso and Rosa, 2005). At 40% NTP, a distinct increase was observed suggesting a phase morphology allowing for the elongation of LLDPE with less interference from a dispersed phase with poor interfacial adhesion. This was further supported by the initial drop in Young's modulus as a result of the small amount of NTP present. However, at about 50% NTP, the modulus slowly increased, suggesting a change in morphology, as discussed earlier.

In the case of compatibilized blends the situation was completely different. The tensile strength dropped gradually from that of LLDPE, but levelled off at about 50% NTP, never dropping below the tensile strength of pure NTP. The elongation at break decreased slowly from that of pure LLDPE, but was improved significantly over that of blends without a compatibilizer. The Young's modulus was less affected by the addition of a compatibilizer. It was concluded that the phase morphology must be the determining factor governing changes in the observed mechanical properties. At low NTP content, sufficient interfacial adhesion leads to high elongation to break values, despite the inclusion of a more brittle NTP phase. As the proportion NTP increased, the elongation did decrease as the blends's behaviour approached that of pure NTP. Based on the tensile strength at high NTP content, it was concluded that NTP must form a continuous phase under these conditions. This would be consistent to previous observation which suggested that as the volume fraction of minor components increases, the morphology would change from a dispersed phase to the continuous phase (Willemse et al., 1998).

## Morphology

Fracture surface of blends with and without PE-g-MAH are shown in Fig 4. Samples without compatibilizer showed two distinct phases at all compositions. It was clear that at low NTP content, NTP formed the dispersed phase with relatively large particles. The incompatibility between the two polymers was suspected to lead to large domains of NTP suspended in LLDPE. At about 50% NTP a dispersed phase was less evident, consistent with observations of improved mechanical properties. However, at high NTP content it appears that LLDPE formed a semi-dispersed phase leading to poor mechanical properties. In all cases where a dispersed phase was observed, a very rough fracture surface was evident with a clear separation between the phases. Poor interfacial adhesion would therefore account for the observed low strength and elongation at break.

At 20 and 30% NTP including PE-g-MAH as compatibilizer, a very large improvement in dispersion was observed. It was difficult to distinguish between different phases and the fracture surfaces appeared much smoother. Some interfacial boundaries were observed as ridges, as indicated in Fig. 6a'. At 40% NTP, a second finely dispersed phase appeared and was thought to an NTP-rich phase. There was no clear separation between these phases, suggesting good interfacial adhesion. This was supported by

earlier observations regarding improved mechanical properties. Above 50% NTP a clear LLDPE phase is evident from ductile fracture regions. NTP appears to have formed a co-continuous phase with LLDPE, but increased NTP phase regions were observed at higher NTP levels (70%).

It was concluded that 10% PE-g-MAH was sufficient to compatibilize NTP and LLDPE. The addition of compatibilizer has reduced the interfacial tension between the phases, increased the surface area of the dispersed phase, improve adhesion and stabilized the phase morphology, consistent with other research (Wang et al., 2004). The mechanism of compatibilizing was thought to be through ester bond formation of anhydride groups in PE-g-MAH and amine groups on protein chains, and chain entanglement between PE-g-MAH and LLDPE.

### **Water Absorption**

Water absorption was carried out in a period of 9 days and the results are shown in Fig. 5. It was found that increasing NTP contents decreased water resistance, evident from substantial water absorption over 9 days. However, including only 30% LLDPE reduced the water absorption from 234% to 31% in blends without a compatibilizer and 45 % in blends with a compatibilizer. Despite the reduction in water absorption by including a hydrophobic polymer, the rate of water absorption was not greatly reduced. It was observed that most water uptake occurred within the first day, regardless the amount of LLDPE added.

### **DMA Analysis**

From Fig. 6, it can be seen that all samples exhibited two glass transition temperatures between that of NTP and LLDPE. LLDPE showed two peaks corresponding to a  $\beta$ -transition at -30 to 10°C and a  $\alpha$ -transition between 30 to 100°C, similar to what has been found by others (Khonakdar et al., 2004, Popli et al., 1984). For 100 % NTP, the  $T_g$  was around 60 to 65°C which is the same region as LLDPE. There was no significant difference between blends with and without compatibilizer, however, the magnitude of the peak in  $\tan \delta$  increased with a decrease in LLDPE contents.

### **CONCLUSION**

As a conclusion, PE-g-MAH has influence on the mechanical properties of NTP/LLDPE blends. The improvements of the tensile strength were strongly marked at 50 – 70 % contents where the tensile properties maintained and did not dropped below the pure NTP strength indicate that there is adhesion between the NTP and LLDPE. It was supported by SEM morphology where the compatibilized blends of NTP have formed a co-continuous phase with LLDPE. Water resistance of NTP itself and the blended materials were substantially improved although DMA analysis shows no significant difference between blends with and without compatibilizer.

**Diagrams, Figures, Tables, Photographs:**

**Table**

Table 1: Formulations of NTP/LLDPE Blends and Control Samples

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

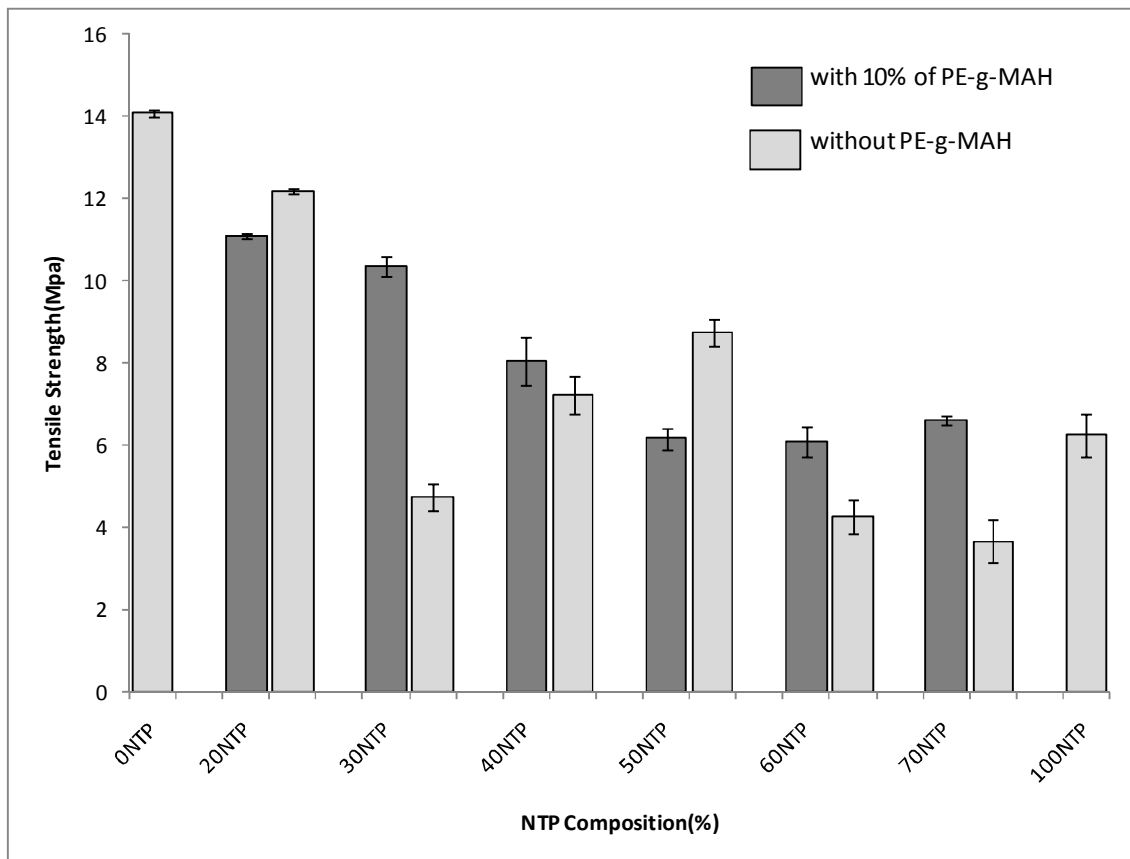
**Figures**

Fig 1: Tensile strength of NTP/LLDPE blends

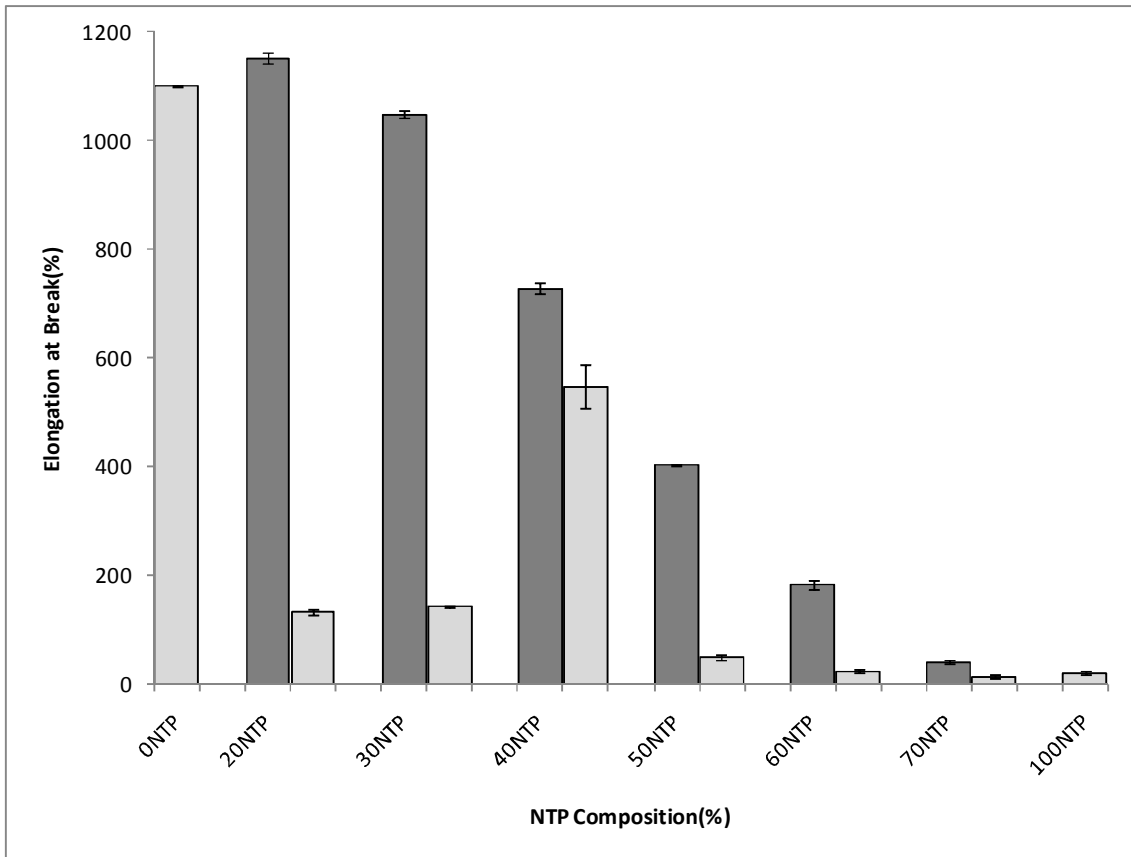


Fig 2: Elongation at break (%) of NTP/LLDPE blends

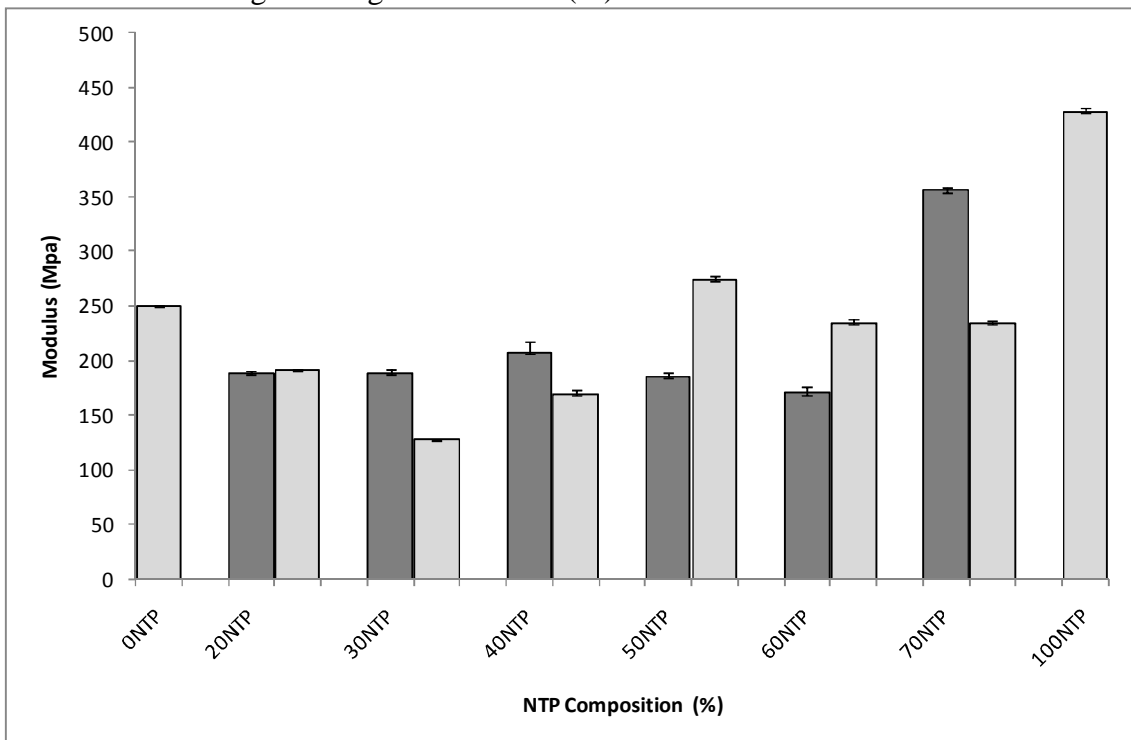
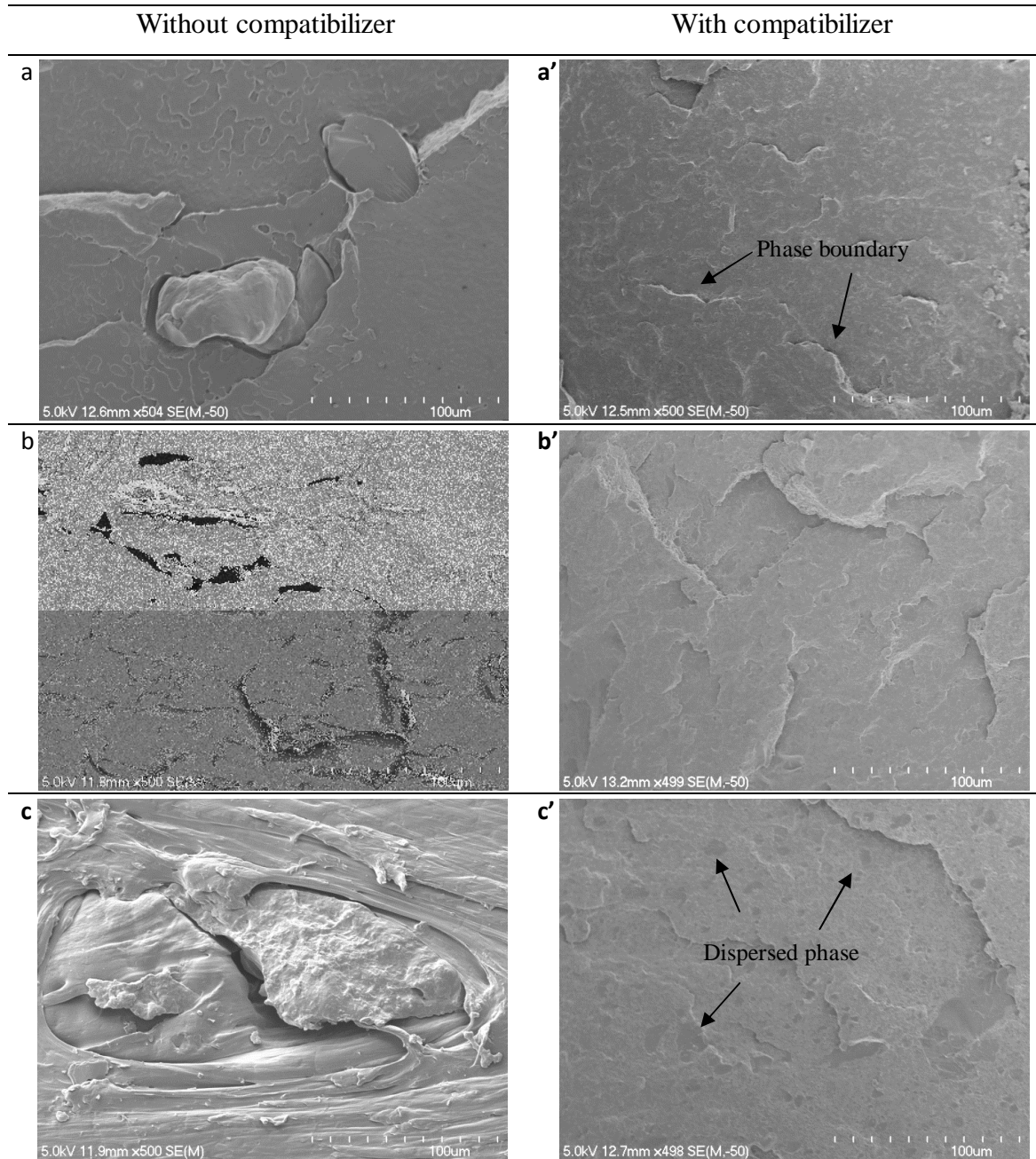


Fig 3: Modulus of various NTP/LLDPE blends





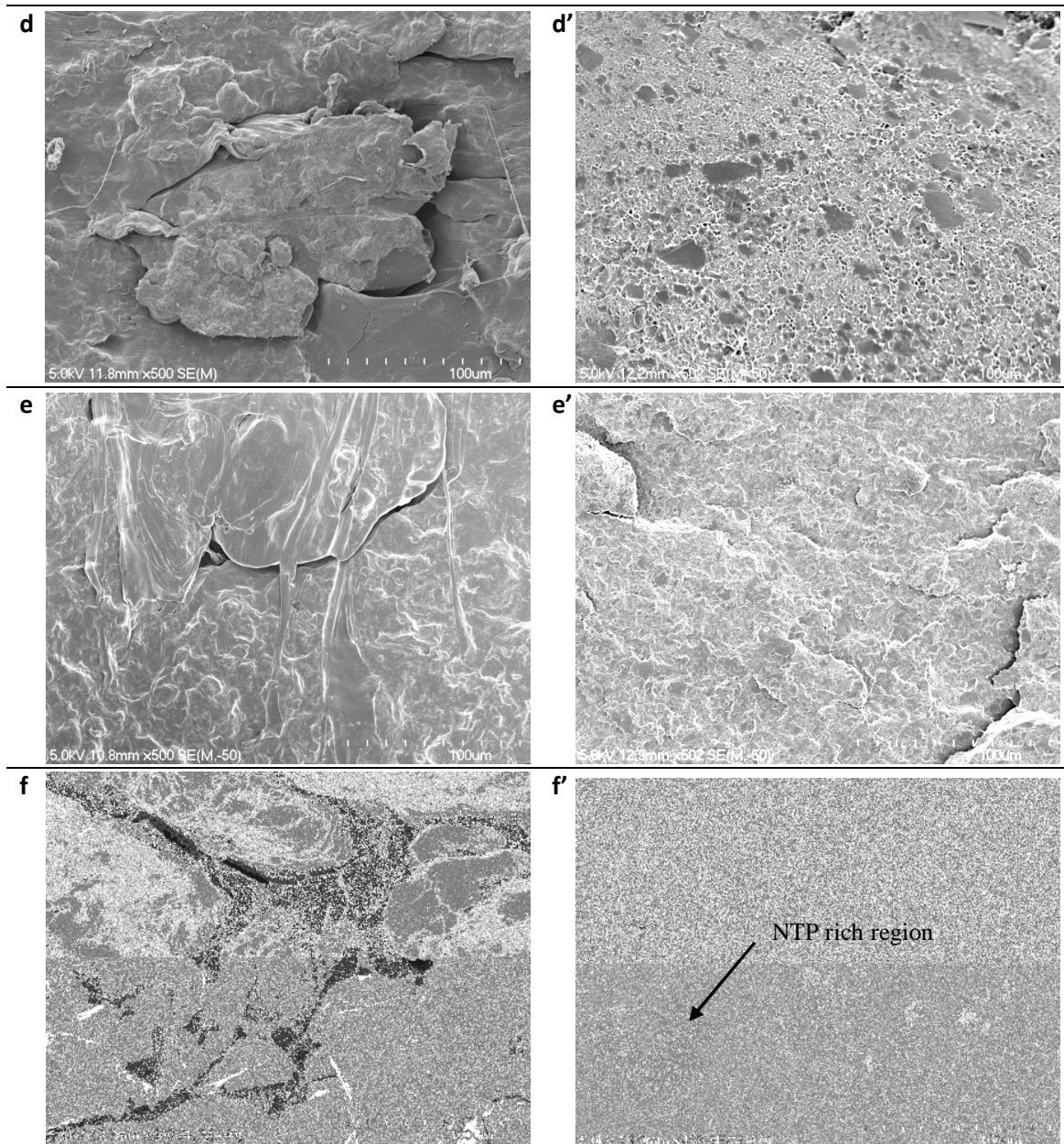


Fig 4: SEM morphology of NTP/LLDPE blends without PE-g-MAH and with PE-g-MAH (a: 20 NTP, b: 30 NTP, c: 40 NTP, d: 50 NTP, e: 60 NTP, f: 70 NTP)

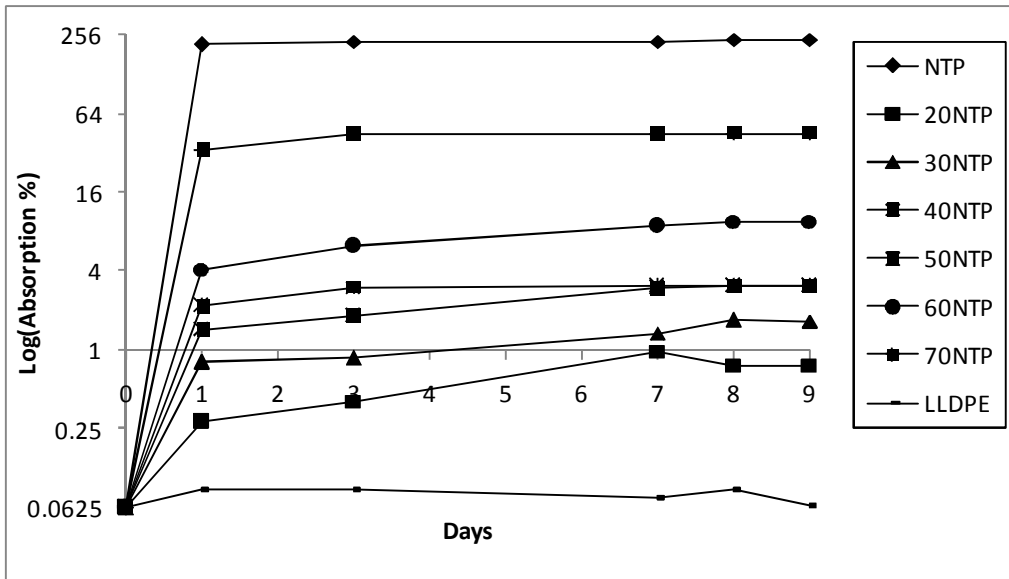


Fig 5: Water Absorption of NTP/LLDPE containing PE-g-MAH

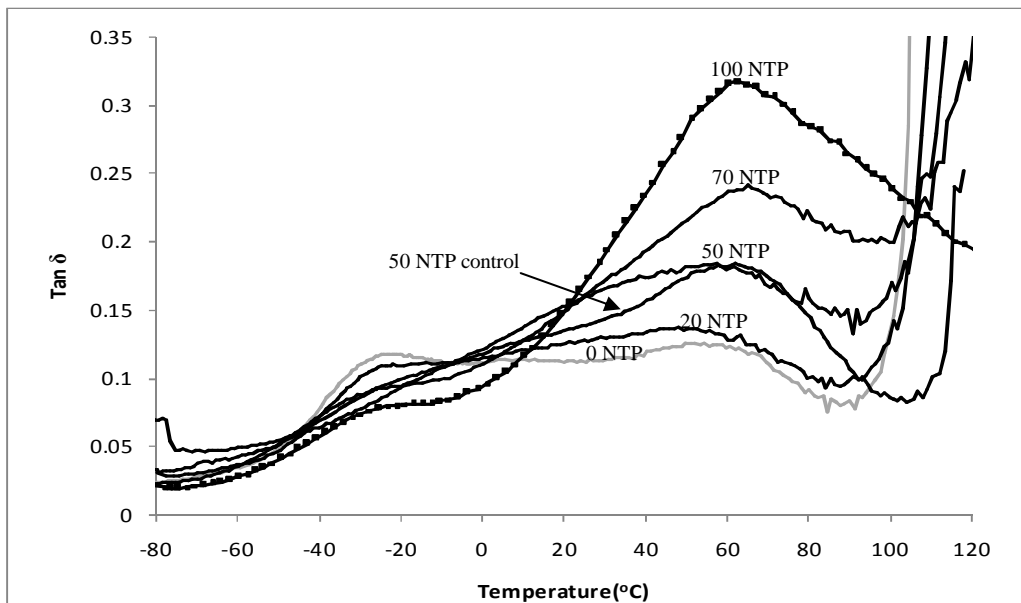


Fig 6: DMA thermogram of compatibilized samples

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