

Effect of Compatibilisers on Thermal and Morphological Properties of Polylactic Acid/Natural Rubber Blends

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In this study, the effects of compatibilisers on morphology, mechanical and thermal properties of polylactic acid (PLA)/natural rubber (NR) blends were determined with the composition of 95/5 (designated as PLA95/NR5). The PLA95/NR5 blend was incorporated with two different compatibilisers maleated polylactic acid (PLA-g-MA) and maleated natural rubber (NR-g-MA) at various loadings (1-10 phr) and compounding was prepared using twin screw extruder. The samples were then characterised using DSC, SEM and DMA. The SEM results showed better interfacial adhesion between PLA and NR phases was achieved upon addition of 3 phr PLA-g-MA. In all cases, further increased PLA-g-MA and NR-g-MA up to 5 phr and 10 phr, respectively in the PLA95/NR5 blend caused the blend stiffness to decrease as decreasing in degree of crystallinity of PLA showed in DSC analysis.

1. Introduction

Polylactic acid (PLA) is known as a biodegradable thermoplastic polymer with widely potential application that has attracted a lot of commercial attention because the polymer is made by fermentation process from 100 % annually renewable resources. PLA advantages and their limitation has been reviewed by Rasal et al. (2010), which can be highlighted as eco-friendly, biocompatibility, processibility high strength and high modulus. High brittleness, poor toughness, slow degradation rate, hydrophobicity and lack of reaction side-chain groups were PLA limitations. To overcome these limitations, PLA was blending with other polymers so-called polymer blend, used a variety of synthetic polymers as a second polymer. These include poly(ethylene) (Anderson et al., 2008), polycaprolactone (Wu et al., 2008) and poly(vinyl acetate) (Gajria et al., 1999). These polymer based petroleum need to be replaced with renewable resource polymer to minimise negative impact to environment. Other elastomers have been reviewed such as thermoplastic polyurethane (TPU), ethylene propylene diene monomer (EPDM) and styrene butadiene (SBR) but these type of elastomer is mainly synthesised from petroleum byproducts.

Interesting material from renewable resource such as natural rubber (NR) has attracted enhanced attention as possible second phase polymer, mainly due to its renewability, high elasticity, flexibility, toughness and low cost. The polymer blend represents a very important field in polymeric materials, which offers better properties in comparison with the neat polymers. The most important controlling parameter in polymer blend processes is degree of compatibility of the blended polymers. Literature reveals that most of polymer blends are incompatible, resulting in materials with coarse morphology, weak adhesion among phases and poor mechanical properties (Anderson et al., 2008). The compatibility between the polymers of a blend can be improved by the addition of compatibilisers which results in a finer and more stable morphology and better adhesion between the polymers of the blend. In this study, grafting maleic anhydride (MA) was used as a compatibilisers due to its good chemical reactivity, low toxicity and low potential to polymerise itself under free radical grafting conditions (Hwang et al., 2012). MA was grafted to PLA and NR to form maleated PLA (PLA-g-MA) and maleated NR (NR-g-MA) that act as compatibiliser. The effects of compatibilisers on morphology and thermal of PLA/NR blends were examined.

2. Materials

The polymer used in this study was a commercial PLA 1323A provided by Shenzhen Esun Industrial Co. Ltd. With a density of 1.35 g/cm^3 and a melt flow index of 7 g/10 min . Natural rubber known as pureprena with the chemical name cis-1,4-polyisoprene was supplied by Malaysian Rubber Board.

3. Blending preparation

The synthesis and characterisation of PLA-g-MA and NR-g-MA were stated in our previous publication (Sani et al., 2014). PLA pellets were dried for 24 h in a dry hopper at $50 \text{ }^\circ\text{C}$, while NR were masticated for 20 min and chopped into small pieces. PLA/NR with compatibilisers was melt blended using a counter-rotating twin screw extruder (Brabender Plasticorder PL 2000) with a temperature profile between 150 to $160 \text{ }^\circ\text{C}$. All the extruded samples were pelletised and compression molded into test specimens for further analysis. The compatibilisers content were varied between 1 to 10 phr (1, 3, 5, 10 phr) meanwhile PLA/NR blends were fixed about 95.5 wt%.

4. Characterisations

4.1 Differential Scanning Calorimetry (DSC)

A DSC (Perkin-Elmer DSC-4) with nitrogen as the purge gas was used to investigate the melting, glass transition and cold crystallisation behaviours of the blends. The sample was heated at a rate $10 \text{ }^\circ\text{C/min}$ from 25 to $200 \text{ }^\circ\text{C}$ then cooled at the same rate from 200 to $25 \text{ }^\circ\text{C}$ and heated again to $200 \text{ }^\circ\text{C}$ (second heating). The glass transition temperature (T_g), cold crystallisation (T_{cc}), melting temperatures (T_m) and percent crystallinity (X_c) were obtained from the second heating scan. $\Delta H_{m \text{ ideal}}$ is the enthalpy of fusion for 100 % crystalline ($\Delta H_m \text{ (PLA)} = 93.7 \text{ J/g}$) (Zhang et al., 2011) was used for crystallisation determination.

4.2 Morphological study

The impact fracture surface of the blends from previous study with similar compositions (Sani et al., 2015) was studied using a JEOL JSM-6301F scanning electron microscope to disclose the distribution and dispersion. The fracture surface was coated with gold to prevent electrostatic charging during examination. An operating voltage of 15 kV and magnification of $2,500\times$ had been used.

4.3 Dynamic Mechanical Analysis (DMA)

Dynamic mechanical properties were measured by a dynamic mechanical analyser (TA Instruments Thermal Analysis) which determines storage and loss modulus. Dimension of samples used for DMA was $50 \times 12 \times 3 \text{ mm}^3$. The DMA test was conducted on a dual-cantilever fixture and the device operated by setting 50 N as static and $\pm 25 \text{ N}$ as dynamic load with a heating rate of $5 \text{ }^\circ\text{C/min}$ in a broad temperature range (-70 to $100 \text{ }^\circ\text{C}$) at a frequency of 1 Hz .

5. Results and Discussion

5.1 Differential Scanning Calorimetry (DSC)

A summary of the T_g , T_{cc} , T_m and X_c data are listed down in Table 1 and 2. The PLA/NR blend has T_g at $55.37 \text{ }^\circ\text{C}$, T_{m1} and T_{m2} of about $147.20 \text{ }^\circ\text{C}$ and $155.03 \text{ }^\circ\text{C}$ and T_{cc} value at $110.87 \text{ }^\circ\text{C}$. The addition of PLA-g-MA has not changed T_g of the PLA. T_m of the PLA/NR blends with the addition of PLA-g-MA is in the range of 154 to $156 \text{ }^\circ\text{C}$ and by adding 3 phr of PLA-g-MA, T_m decreased to $154.53 \text{ }^\circ\text{C}$ but T_m starts to increase again may cause by increase of molecular weight and led to decrement of chain mobility as PLA-g-MA was increased to 5 and 10 phr. This trend is also applicable for T_{cc} . The degree of crystallinity, X_c of PLA/NR blends only showed a slightly decreasing with the addition content of PLA-g-MA up to 3 phr. This may be attributed by poor blending during processing system or characterisation of material. In addition, this irregular chain branching of MA onto the PLA backbone might decrease regularity and hinder the crystalline growth of PLA, resulting in lower crystallinity. The modification of PLA to get long and branched structures by using chain extender like MA is an efficient approach to control the thermal properties (Al-Itry et al., 2012). By incorporating with NR-g-MA, the T_g , T_m , and T_{cc} shows a decrement as the content of compatibiliser increase up to 3 % and starts to remain constant thereafter. As NR-g-MA was more to amorphous component due to its rubber content, the addition of NR-g-MA led to a decrease in the crystallinity of the blend. This result may be attributed to the presence of NR-g-MA at the PLA/NR interface that may prohibit the crystal formation and delay the crystallisation temperature.

Table 1: Thermal characteristics of PLA/NR/PLA-g-MA blends

Designation	T_{m1} (°C)	T_{m2} (°C)	T_{cc} (°C)	T_g (°C)	X_c (%)
PLA95/NR5	147.20	155.03	110.87	55.37	26.00
1 phr PLA-g-MA	147.20	155.20	109.87	56.26	25.05
3 phr PLA-g-MA	146.70	154.53	109.37	56.26	17.50
5 phr PLA-g-MA	147.37	155.37	110.37	56.15	24.65
10 phr PLA-g-MA	147.70	155.87	110.03	55.92	22.50

Table 2: Thermal characteristics of PLA/NR/NR-g-MA blends

Designation	T_{m1} (°C)	T_{m2} (°C)	T_{cc} (°C)	T_g (°C)	X_c (%)
PLA95/NR5	147.20	155.03	110.87	55.37	26.00
1 phr PLA-g-MA	146.53	154.70	109.53	54.53	25.06
3 phr PLA-g-MA	143.20	152.70	102.03	52.31	26.28
5 phr PLA-g-MA	146.87	155.03	109.53	56.13	24.74
10 phr PLA-g-MA	146.87	155.20	109.20	55.13	22.70

5.2 Morphological Study

Figure 1 shows the SEM micrograph of PLA/NR blends filled with PLA-g-MA and NR-g-MA compatibiliser (with mag.2500X) taken from the impact fractured surface. The rough fracture surface can be seen clearly. All micrographs had rubber particles with different sizes and different distribution. From uncompatibilised PLA/NR blend micrograph, it can be seen that poor adhesion between NR particles and PLA matrix were noted from the fracture surface where NR particles pulled from the matrix. The easy detachment of NR from the PLA matrix indicated a very weak interfacial adhesion between NR and PLA. With addition of 3 phr PLA-g-MA, PLA matrix and NR phase showed a more homogeneous fracture surface which indicating the presence of interaction and better adhesion between NR and PLA phase. The blending having higher amount of PLA-g-MA which indicated the increment of MA may lead to agglomeration and the size of NR phase became slightly larger as shown in Figure 1. Because of that, the applied stress could not be transferred through the interface between polymers, which in turn resulted in a limited improvement in mechanical properties (Sani et al., 2015). From previous discussion on mechanical properties, addition of NR-g-MA tends to decrease the quality of the properties (Sani et al., 2015). Figure 1 showed that the blends had poor dispersion and distribution of particles which led to the agglomeration of NR as the amount of NR increased along with NR-g-MA content. The interfacial adhesion between the PLA and NR becomes very weak.

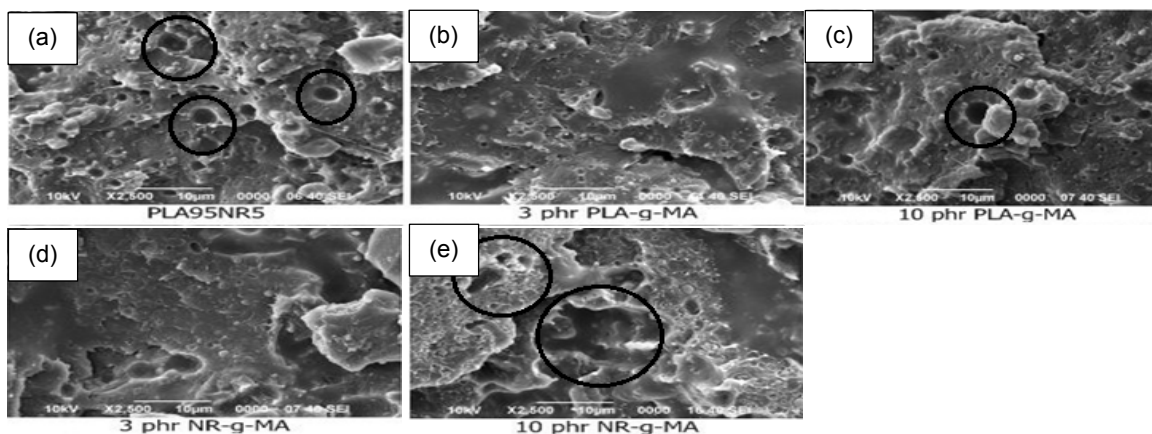


Figure 1: SEM micrographs of PLA/NR/PLA-g-MA blends: (a) PLA/NR, (b) 3 phr PLA-g-MA, (c) 10 phr PLA-g-MA, (d) 3 phr NR-g-MA and (e) 10 phr NR-g-MA

5.3 Dynamic Mechanical Analysis (DMA)

The storage modulus (E'), loss modulus (E''), and the $\tan \delta$ versus temperature for the PLA/NR blends are shown in Figures 2, 3, 4. From Figure 2(a), a gradual decline in E' for compatibilised PLA-g-MA with increasing temperature from -70 °C to 90 °C was observed when comparing with PLA/NR blends. The glass transition of the PLA started from 65 °C to 75 °C while the glass transition of the NR started from -60 °C to -40 °C. The storage modulus decreased sharply around the glass transition temperature of the PLA and matched

to the onset of chain mobility. Comparing PLA/NR with PLA/NR/PLA-g-MA, the storage modulus decreased with further increment of PLA-g-MA content. It indicates that the elastic properties were reduced by addition of PLA-g-MA. Both compatibilised PLA-g-MA and NR-g-MA blends showed decrease in storage modulus with further addition of compatibiliser. This indicates that the stiffness of the blends was decreasing with the addition of large amounts of MA and led to decrease in degree of crystallinity of the blends as in agreement with the static mechanical test discussed earlier (Sani et al., 2015).

Figure 3(a) represent the temperature dependence of E'' for the blends containing various amounts of PLA-g-MA. It shows that the loss modulus of the blends at the peak point around $\approx 70^\circ\text{C}$ was higher with the addition of compatibiliser. It is shown that 3 phr is the highest peak, followed by 1 and 5 phr. Meanwhile for 10 phr compatibiliser, the peak was lower than PLA/NR without compatibiliser. This could be the decrement of properties as much compatibiliser was added and led to inhomogeneous system. Addition of NR-g-MA in Figure 3(b) mainly affected at temperature around $\approx -50^\circ\text{C}$ which is the glass transition temperature for natural rubber due to the increases of NR. It is found that the peak points in that region were increased by increasing the amount of compatibiliser. It is clearly shown that 10 phr had the highest peak, followed by 5, 3 and 1 phr. At peak around $\approx 70^\circ\text{C}$, the value of E'' for NR-g-MA blends was lower than uncompatibilised PLA/NR. This may cause NR-g-MA compatibiliser contributed more natural rubber mechanism than other type of compatibiliser as NR has lower T_g and less force is required for deformations.

From the Figure 4(a), it was discovered that the temperature of maximum $\tan \delta$ of the blends increased with increasing PLA-g-MA content. This temperature is the α transition temperature (T_α) and is equivalent to the glass transition temperature (T_g) determined from the differential scanning calorimetry (DSC) analysis. T_α is higher than T_g from DSC because of different testing parameters. Dynamic load was applied during DMA analysis while DSC only used heating. One peak that can be seen clearly at 74°C corresponds to glass transition temperature of PLA (Zhang et al., 2013). PLA/NR blends showed a sharp and high damping peak compared to compatibilised PLA/NR which displayed broad and low peaks. A high damping peak was observed for PLA/NR due to unrestricted to the motion of the free chain segment (Liu et al., 2007). A broader and lower damping peak in the transition zone is subsequent of the compatibiliser that restricts the motion of the matrix chain, thereby affecting the relaxation of the matrix chain (Zhang et al., 2006). According to Somdee (2009), the higher the height of $\tan \delta$ peak, the more energy is dissipated. The $\tan \delta$ peak recorded for the blends shifted to higher temperatures compared with the $\tan \delta$ peak for PLA/NR. This indicates that there is an improvement in the interfacial adhesion between NR and the PLA matrix due to the addition of PLA-g-MA. A similar observation was discussed by Petersson et al. (2006) who used PLA-g-MA as a compatibiliser in PLA/Layered-Silicate nanocomposites. From Figure 4(b), addition of NR-g-MA leads to the increases of NR content. As the rubber content increases, an increase at temperature peak around -60°C to -40°C was observed. Rubber has affected the damping behavior and increase the damping because of its rubbery nature and the flexible rubber chains respond rapidly towards cyclic loading (Komalan et al., 2007). This was expected because NR is a flexible polymer and is rubbery in the glass transition range.

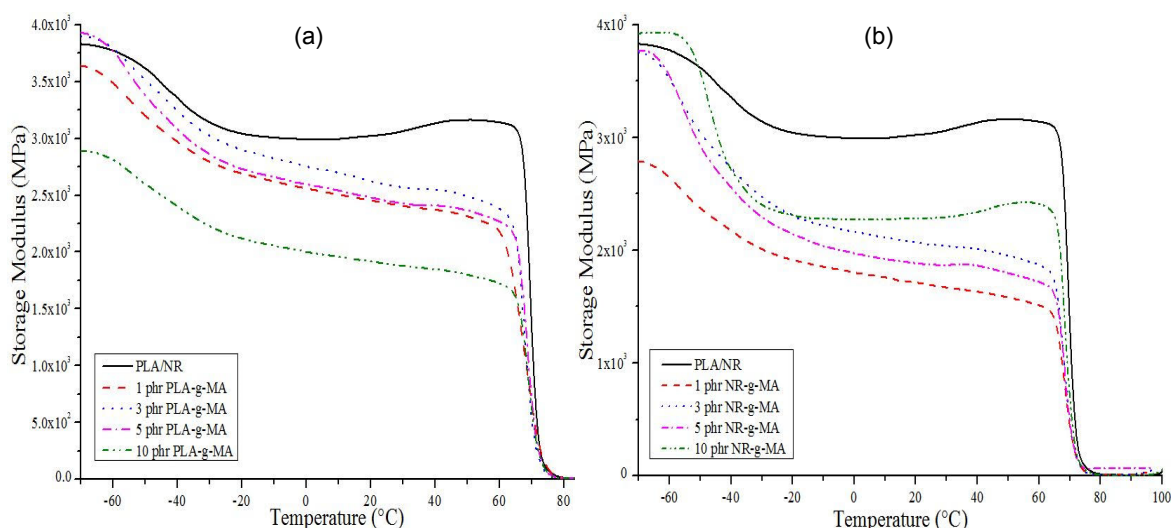


Figure 2: The storage modulus vs. temperature obtained from DMA of PLA/NR and the blends: (a) PLA-g-MA, (b) NR-g-MA

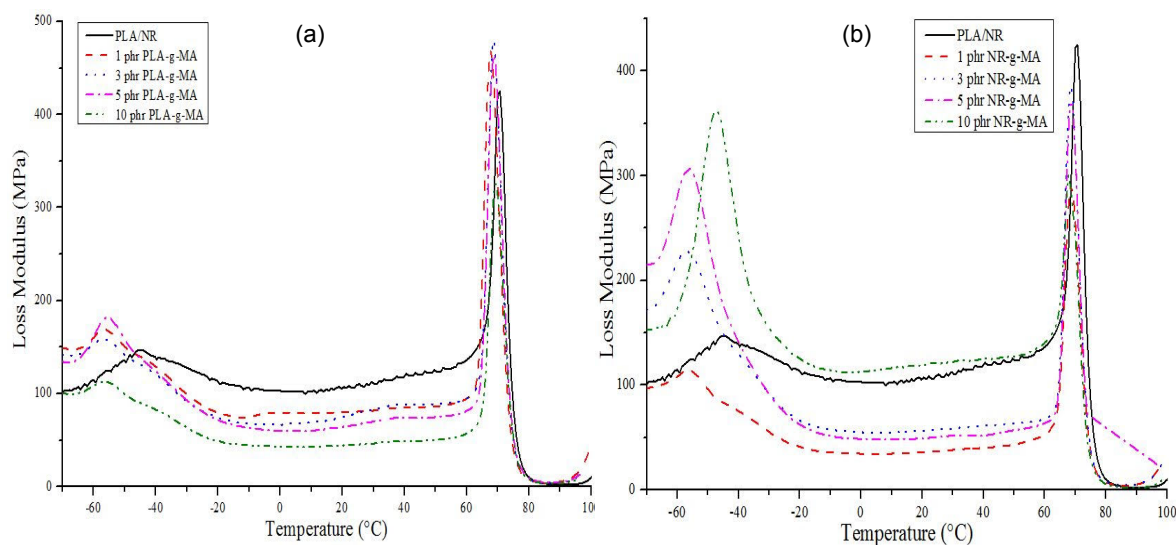


Figure 3: The loss modulus vs. temperature obtained from DMA of PLA/NR and the blends: (a) PLA-g-MA, (b) NR-g-MA

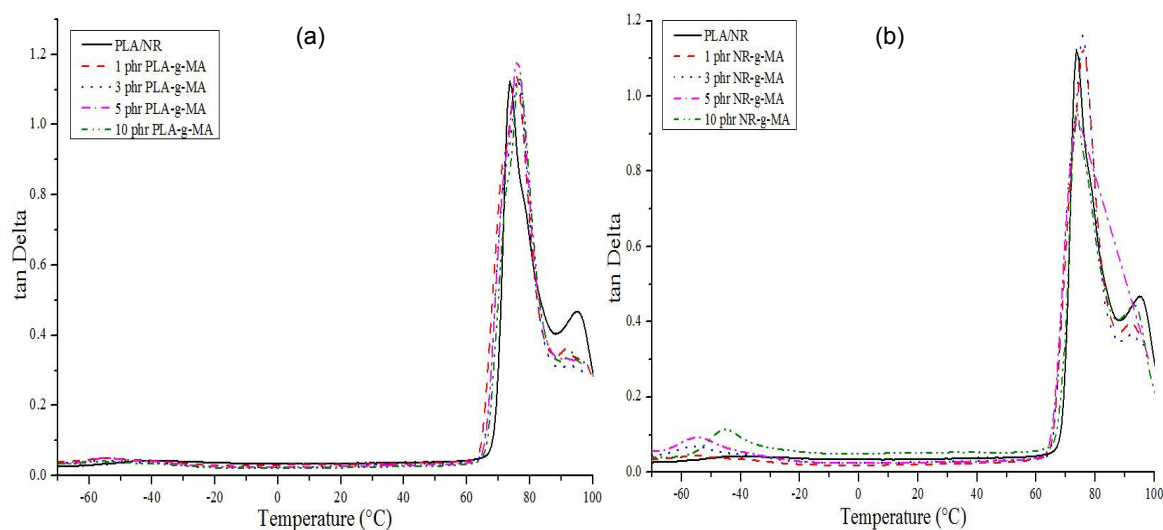


Figure 4: The $\tan \delta$ vs. temperature obtained from DMA of PLA/NR and the blends: (a) PLA-g-MA, (b) NR-g-MA

6. Conclusion

In this study, DSC results revealed the melting points of both blends remain roughly unchanged while the crystallisation temperature of the blends slightly decreased. SEM results indicated that the addition of PLA-g-MA increased the interfacial adhesion between PLA and NR phases, leading to ductile behavior but result in agglomeration of NR when the blending was at higher amount of compatibilisers. DMA study showed that 3 phr PLA-g-MA exhibited the highest value of storage modulus and with further addition of compatibiliser, the stiffness of the blends was decreased which indicated that the elastic properties were reduced by addition of PLA-g-MA and also NR-g-MA. As the result, PLA-g-MA has played a good role as compatibiliser compared to NR-g-MA according those analyses. The effective composition of PLA-g-MA was 3 phr as it was showed better performance towards PLA properties compared to others formulations.

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