STRUCTURE AND PROPERTIES OF POLYLACTIDE/NATURAL RUBBER BLENDS

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ABSTRACT

Polylactide, PLA, is a biodegradable thermoplastic polyester derived from biomass that have restricted packaging applications due to its high brittleness and poor crystallisation behaviour. Here, new formulations based on natural rubber-PLA blends have been developed. The processing windows, temperature, time, and rotor rate, and the rubber content have been optimised in order to obtain a blend with useful properties. The rubber phase was uniformly dispersed in the continuous PLA matrix with a droplet size range from 1.1 to 2.0 μm . The ductility of PLA has been significantly improved by blending with natural rubber, NR. The elongation at break improved from 5 % for neat PLA to 200 % by adding 10 wt% NR. In addition, the incorporation of NR not only increased the crystallisation rate but also enhanced the crystallization ability of PLA. These materials are, therefore, very promising for industrial applications.

Keywords: Biopolymers; immiscible blends; microstructure

1. Introduction

Recently, biodegradable polymers derived from natural resources have gained much interest as they can be an alternative to petroleum based polymeric materials as well as a solution to waste disposal problems. Thus, the development of such materials is a crucial issue in order to reduce the environmental impact of plastic production and waste.

One of these biomaterials is the polylactide (PLA). PLA is a biodegradable thermoplastic polyester derived from biomass such as sugar, corn, beet, which possesses excellent physical and mechanical properties combined with biocompatibility and biodegradability properties [1]. Due to its initial production costs, the starting applications of PLA have been focused on high value products such as medical devices [2]. On the other hand, PLA's potential for food packaging is very high due to its transparency, mechanical properties and acceptable moisture processability for dry food stuff [3-5]. Nevertheless, there are some drawbacks, such as its high brittleness and poor crystallisation behaviour that limit its current use in food packaging [6, 7]. In order to overcome these limitations, the copolymerization of lactides with other monomers has been a widely used approach, but without any success for commercial application [8-10]. A less expensive and more practical strategy to overcome these drawbacks is the blending of PLA with other polymers. Hence, several synthetic polymers, such as low density poly(ethylene) [11], poly(propylene glycol) and poly(ethylene glycol) [12, 13], polymeric plasticizers [14, 15], or biodegradable polymers such as polycaprolactone [16-18], poly(butylene succinate) [19], poly(butylenes adipate)-co-terephthalate [20], and poly(ethylene succinate) [21] have been used. However, most of these blends are incompatible and compatibilisers are required in order to attain the desired properties. In addition, most of these polymers are not biocompatible which limits its applications.

On another hand, rubber matrices have commonly been used as a second phase polymer to improve the toughness of brittle thermoplastic materials. The rubber particles behave as stress

concentrators enhancing the fracture energy absorption of brittle polymers and ultimately results in a material with improved toughness. In order to impart toughness to polymers, several criteria must be met: the rubber must be distributed as small domains in the polymer matrix, the rubber must have good interfacial adhesion to the polymer, the glass transition temperature of the rubber must be at least 20 °C lower than the use temperature, the molecular weight of the rubber must not be low, the rubber should not be miscible with the matrix polymer, and the rubber must be thermally stable in the polymer processing temperatures [22-24].

To date, however, the physical and mechanical properties of PLA/rubber blends have received little attention and, to the best of our knowledge, natural rubber (NR) has never been used for toughening PLA [25-28]. Natural rubber is a renewable resource derived from a milky colloidal suspension or latex found in the sap of some plants. It exhibits a unique combination of toughness, flexibility, biocompatibility and biodegradability that together with its low cost makes it an ideal candidate to improve the brittleness of PLA [29,30].

For the above mentioned, this study aims to improve the physical and mechanical properties of PLA by blending it with natural rubber and, thus optimise the material for specific end use applications. The processing conditions, compatibility, phase morphology, crystallisation, rheological and mechanical properties of PLA/NR blends were assessed.

2. Experimental Part

2.1 Materials and sample preparation

PLA was provided by NatureWorks®. The selected grade, PLA 2002D (D-content 4.25 %, MI = 5-7 g/10 min) is a semicrystalline extrusion material with a residual monomer content of 0.3%. It was dried overnight at 80 °C prior to use in a desiccating dryer. Natural Rubber (NR)

was kindly supplied by Malaysian Rubber (Berhad, Malaysia) under the trade name CV60 (Mooney viscosity: $ML(1 + 4)_{100\text{ }^{\circ}\text{C}} = 60$).

PLA/NR blends were prepared by melt blending in a Haake Rheomix 9000 internal mixer, a Haake Minilab twin screw extruder was also used. The optimal processing conditions were selected in order to obtain the best compatibility of the polymer phases. Subsequently, the materials were compression-moulded into 0.4 mm thick sheets in a Collin P200P press for mechanical testing and rheological measurements. The samples were initially compressed at 10 bars at 170 °C for 2 min, then at 150 bars for 2 min and were finally cooled under pressure (150 bars) for 2 min.

2.2 Structural Characterisation

The determination of PLA molecular weight was performed by Size Exclusion Chromatography (SEC) in CHCl_3 (3 ml/min) at 30 °C using a HPLC Perkin Elmer setup, made of a pump series 200, a refractive index detector series 200a, a column oven series 200, a network chromatography interface NCI 900 COLUMN. Calibration was performed using narrow distributed polystyrene standard.

Measurements of the refractive indices of the materials have been carried out using an Abbe refractometer from Atago. 1-bromonaphthalene was used as a contact liquid and at least 6 specimens of each film were tested to determine a mean value of the results.

The morphology of the samples was observed using a Philips XL30 environmental scanning electron microscopy (ESEM) at 15 kV. All the samples were cryo-fractured after immersion in liquid nitrogen and the fracture surface was sputter coated with gold/palladium (Au/Pd 80/20) in order to prevent electrical discharge during observation. The rubber droplet size was determined by image analysis (ImageJ software, Rasband, W.S., ImageJ, U. S. National Institutes of Health, Bethesda, Maryland, USA, <http://rsb.info.nih.gov/ij/>, 1997-2009).

Typically, 200 droplets were analysed per sample and the average Feret's diameter was calculated.

The crystallisation process was examined in a Mettler Toledo DSC822 differential scanning calorimetry. The following procedure was adopted: samples of about 10 mg were firstly heated from room temperature to 180 °C at a scan rate of 10 °C/min to erase the thermal history, then they were rapidly cooled to -90 °C, and, finally a second heating scan from -90 °C to 200 °C at 10 °C/min was carried out. The experiments were performed in a nitrogen atmosphere.

The crystallisation behaviour of PLA was also monitored in an optical polarising microscope (Carl Zeiss Amplitval microscope) equipped with a Linkam THMS 600 automatic heating and freezing stage thermal control. Samples were sandwiched between microscope cover slips and isothermal crystallisation at 130 °C from melt state was studied.

2.3 Gas chromatographic analysis

Experiments were performed using a 6890N gas chromatograph equipped with a mass spectroscopic detector from Agilent, an injecting system from Industrie Laboratoire Service and a HP-5ms column. He was used as carrier gas and samples were heated from 60 °C to 315 °C at 30 °C/min. The identification of the compounds was made by comparison of their mass spectra with the SDBS data base.

2.4 Rheological analysis

The rheological measurements were performed using an Advanced Rheometer AR1000 from TA Instrument with parallel plate geometry of 20 mm of diameter. Tests were carried out in dynamic mode of shearing at 160 °C from 0.01 Hz to 100 Hz frequency range. The experiments were performed in the linear viscoelasticity domain (torque 50 mN.m).

2.5 Mechanical properties

Tensile tests of the samples were measured according to ASTM D 3379-75 specifications on an Instron dynamometer (model 3366) at 23 °C, and at a cross-head speed of 10 mm/min. Dogbone-style samples were prepared from the sheets obtained by compression-moulding. At least five specimens of each sample were tested to determine a mean value of the results.

3. Results and Discussion

3.1 Optimisation of the processing window

3.1.1 *Morphology of the blends*

Most polymers are not miscible with other polymers as both entropy and enthalpy factors are usually unfavourable which leads to heterogeneous systems with a multiphase morphology. However, numerous two phase systems have very useful properties. The properties of the blend are not only dependent on the physical properties of each component but also on the dispersed phase microstructure and the interfacial chemistry [31]. To attain a desired benefit, it is necessary in this study to optimise the processing conditions in melt state as it will affect the morphology and the physical properties of the materials. Melt processing is the procedure generally used for preparing polymer blends. During processing, the components are melt-blended, and the minor phase is broken up to form the dispersed phase. Several factors, such as temperature, time, and rotor rate must be considered in order to obtain a blend with useful properties. In our case, the processing window is evaluated for PLA/NR blends setting the rubber concentration at 10 wt%. One of the drawbacks of PLA melt processing is its low thermal stability that readily undergoes random main chain scission. So, the first parameter to study is the temperature.

Three blends were prepared at different temperatures, 160, 180 and 200 °C, while the rotor rate and blending time were fixed at 60 rpm and 15 min, respectively. **Figure 1** shows the ESEM micrographs of the fracture surfaces of PLA/NR blends. All the blends showed phase

separated morphology where the rubber particles formed small dispersed droplets with low interfacial adhesion with the PLA matrix, which constituted the continuous phase. We observed an increase of the NR average droplet size with increasing temperature (**Table 1**). Also, the dispersion of the droplet size became broader.

Several studies of the morphology of immiscible blends have been performed to understand the effects of the processing parameters. A correlation was proposed by Wu for extruded polymer blends relating the average diameter of the dispersed phase (d) to the viscosity ratio (K) of the dispersed phase (η_d) to the matrix viscosity (η_m), the shear rate ($\dot{\gamma}$) and the interfacial tension (α) [32]:

$$d = \frac{4\alpha K^{\pm 0.84}}{\dot{\gamma} \eta_m} \quad (1)$$

The exponent of K is negative for $K < 1$ and positive for $K > 1$. Other authors modified this equation taking into account the effect of the dispersed phase concentration, or considering that the average diameter is not exactly an inverse function of the shear rate [33, 34]. Thus, decreasing the matrix viscosity by increasing the temperature will result in an increase of the average droplet size of rubber domains in the blend. Moreover, a decrease of the viscosity of the matrix facilitates the coalescence of the droplets of the dispersed phase as the contact time required for drop coalescence is lower [35].

The influence of rotor speed and mixing time over blend morphology were also studied. Three rotor speeds (30, 60 and 90 rpm) and two mixing times (10 and 15 min) were tested. However, it appeared that these parameters hardly varied the blend morphology (**Table 1**). Similar results have been reported in the literature, for instance see ref. [36, 37]. Thus, we chose to fix the rotor speed at the intermediate value of 60 rpm and the blending time at 15 minutes. The mechanical properties suggested that the samples prepared under these conditions were more homogeneous as the standard error was less than 5 % (data not shown).

3.1.2 PLA degradation

It is well known that one of the limitations of PLA towards its wider industrial application is the thermal and mechanical degradation that suffers during processing. Chain length reduction by hydrolysis or alcoholysis reactions strongly depends on traces of residual monomer, water or residual organometallic compounds used during polymerisation [38]. Hence, it is very important to consider PLA degradation during processing. For this purpose, PLA was processed alone at 160 °C for 15 min and at a rotor rate of 60 rpm. Its possible degradation during melt processing was evaluated by viscosity measurements and resulted in a significant decrease of the complex viscosity after processing from 21.0×10^3 Pa·s to 6.3×10^3 Pa·s. This decrease suggested a clear reduction of the molecular weight of approximately 30 % due to chain scission processes, according to the relation $\eta_0 = KM_w^{3.7}$. The results were confirmed by SEC as the average molecular weight of PLA shifted from 13.6×10^4 to 9.0×10^4 after processing.

Later, we evaluated the influence of this molecular weight reduction on crystallisation and mechanical properties of PLA. Isothermal crystallisation was studied by polarised optical microscopy (**Figure 2**): the samples were melted at 180 °C for 2 minutes and cooled to 130 °C at 30 °C/min and photos were taken at different times of isothermal treatment. We observed the development of spherulites after 30 min in the case of pristine PLA compared to 10 minutes in the case of processed PLA. This result shows that processing can induce a significant increase of crystallisation rate due to the presence of smaller chains. [39,40]. However, no significant changes on the mechanical properties of PLA as a function of processing were observed. (see discussion on mechanical properties)

Moreover we should also consider that the addition of NR to PLA could have a certain influence over PLA degradation during processing. To highlight this effect, the blends were

carried out in a twin-screw extruder where the surface effects are more pronounced than in the internal mixer. **Figure 3** shows the evolution of torque in the extruder during blending for pure PLA and PLA/NR 10 wt% blend. An important reduction of torque and extrusion pressure is observed. It appeared that NR acted as a lubricant for the blend, limiting friction effects and local overheating, and thus could limit PLA degradation. To confirm this observation, NR phase was removed from the blend by dissolving selectively PLA from the blend using dioxane as a solvent. The solution was then filtered to remove NR droplets and dried under vacuum. An average molecular weight of 11.6×10^4 was then obtained for PLA in PLA/NR 10 wt% blend confirming the limited degradation of PLA.

To explain this effect of NR, we should consider the complex formulation of NR [41]. Natural rubber contains a non negligible amount of lipids, proteins and fatty acids derived by hydrolysis of phospholipids during storage, and these small molecules can easily migrate to the surface [42]. This migration was evaluated by a simple experiment: the blend was immersed in acetone for few minutes at the outlet of the extruder, and the acetone, which is a non solvent for both PLA and NR, was then analysed by GC-MS. **Figure 4** shows the mass spectra of the acetone at various retention times. Molecules of isoprene as well as lactide (residual monomer) and oligomers of PLA were identified at retention time of 8.5 and 8.2 min, respectively. We also identified molecules of fatty acids such as palmitic acid and linoleic acid at retention times of 5.9 and 6.5 min, respectively. These molecules were not observed in the case of NR extracted with acetone prior to mixing. The migration of small molecules at the surface of the blend acting as a lubricant during processing was then confirmed.

3.2 Effect of Natural Rubber concentration

3.2.1 Morphology

We analysed the effect of the NR concentration on the morphology of the blend. Hence, we prepared three blends at 5, 10 and 20 wt% of natural rubber. It is of interest to note that transparency of the blends is not completely lost (**Figure 5**). Refractive indices of 1.4537 ± 0.0013 , 1.5209 ± 0.0008 and 1.4579 ± 0.0013 have been measured for PLA, NR and PLA/NR 10 wt% respectively and are in agreement with those reported in the literature [3,43]. Even though the refractive indices of PLA and NR are quite different, the addition of 10 wt% of NR to the PLA matrix only results in a slight increase of the refractive index of the blend. The addition of NR produces only a slight yellowish coloration of the blend and translucent material is obtained at low thickness.

Figure 6 shows the ESEM micrographs of the fracture surfaces of PLA/NR blends. It is worth to note that the size of the rubber particles is similar in the case of PLA/NR 5 wt% and 10 wt% but increased for a concentration of 20 wt% from 1.15 to 2.03 μm (**Table 1**). In general, in an immiscible binary polymer blend, the size of the dispersed phase increases as a function of the concentration of the minor phase in the blend, due to coalescence phenomena [35]. At high concentrations, the dispersed phase will lead to the development of a phase inversion. It is well known that the particle size in blends with dispersed structure is governed by the competition between their breakup and coalescence. Several theoretical and experimental approaches in homogeneous steady shear or extensional flow have been developed to predict the final blend morphology [34]. However, flow field in internal mixers is not homogeneous and the stress varies in different areas. Small drops can appear in high shear regions due to break-up, while increased droplet interactions at high concentration of the dispersed phase will result in large drops due to coalescence, resulting in a broader distribution size. So, the distinction of both phenomena, break and coalesce, in mixers is a complex issue.

3.2.2 Crystallisation behaviour

Figure 7 shows the DSC heating curves of PLA/NR blends. The results confirmed the immiscible behaviour of the blends since no changes were observed in the glass transition temperature (T_g) of PLA with the NR content. Interestingly, we observed a cold-crystallisation exothermic peak and a melting endothermic peak in both 10 wt% and 20 wt% PLA/NR blends (**Table 2**). These results suggested that the incorporation of NR enhanced the crystallisation ability of PLA. Similar results were reported by Li et al. for PLA/PU blends [28].

The isothermal crystallisation of the blends was further analysed via rheological measurements. This study was motivated by the extremely low crystallisation rate of PLA, which results in a low heat flow often within the DSC equipment resolution limits [44]. Khanna was the first to use rheological measurements to determine polymer crystallinity and since then this technique has been used on a wide range of systems [45-46]. Small increments in the polymer crystallinity result in an increase of complex viscosity due to both the filler effect of the crystals and the physical crosslink and retardation effect of the polymer chains within the entangled system [44]. For our experiments, the blends were melted inside the rheometer at 180 °C for 2 min to erase thermal history and then quenched at 120 °C. The evolution of complex viscosity was then monitored as a function of time. Tests were carried out at 1 Hz and within the linear viscoelasticity domain at small strain values to avoid shear-induced crystallisation. It should be noted that the linear viscoelasticity domain evolves as the samples crystallised and that it is very difficult to carry out the measurements until complete crystallisation of the samples. **Figure 8** represents the evolution of the ratio of the measured viscosity to the initial viscosity of the blends. It is clearly observed that the addition of NR increases PLA crystallisation rate confirming the nucleating effect of NR over PLA. Similar behaviour of PLA crystallisation has been reported in other thermoplastic-PLA blends [19,

48]. The crystallisation behaviour of a crystallisable matrix in immiscible blends can be affected by two major phenomena which are the migration of impurities during melt-mixing and the nucleating activity of the interface [49]. In our case, we previously observed migration of small molecules from the NR phase which could act as nuclei for PLA. As the concentration of NR increases in the blends, the amount of nuclei that can migrate varies as well and the nucleation density in the crystallisable phase increases. However, we also observed that increasing the NR concentration results in the formation of larger droplets and thus in a lower total interfacial contact area. Two phenomena are then in competition the increase of nuclei able to migrate and the reduction of contact area between the two polymers. In our case, it appears that the increase of nuclei concentration is the predominant effect.

The crystallisation degree of the samples fully crystallised in the rheometer was then determined by DSC. **Figure 9** represents the first heating scan of the crystallised blends at 10 °C/min. The slight increase of crystallinity is attributed to the nucleating effect of NR (**Table 3**). A decrease of few degrees of the melting temperature with NR concentration could attest to the formation of smaller spherulites due to the migration of impurities from NR to PLA [50].

3.2.3 Rheological properties

The rheological study of the blends is of crucial importance to understand the processability of materials. Moreover, composition and morphology are directly reflected on rheological properties. **Figure 10** shows the viscoelastic behaviour of PLA, NR and PLA/NR blends. PLA followed the characteristic terminal zone behaviour, i.e. $G' \propto \omega^2$ and $G'' \propto \omega$ with a zero shear viscosity of 6×10^3 Pa·s while NR showed a low dependence of complex shear modulus with frequency in the terminal flow zone. If we now consider PLA/NR blends, the absolute value of the complex viscosity $|\eta^*|$ increased with the concentration of NR in the

terminal zone, as well as the storage modulus G' and the loss modulus G'' . More interestingly, a secondary plateau is observed for the blends with a NR concentration of 10 wt% and 20 wt%, which can be attributed to a new relaxation phenomenon. The Cole-Cole diagram (Figure 9d, $\eta'(\omega)$ vs $\eta''(\omega)$) clearly shows two relaxation mechanisms for PLA/NR 10 wt% and 20 wt% blends. The first one, at high frequencies, is attributed to the PLA matrix with a relaxation time λ_m of 0.3 s. The characteristic times of the secondary plateau are estimated to be 25 s and 100 s for PLA/NR 10 wt% and PLA/NR 20 wt%, respectively, and are attributed to the droplets relaxation time [51, 52].

3.2.4 Mechanical properties

The tensile behaviour of the materials is shown in **Figure 11** and **Table 4**. PLA is a rigid and brittle polymer with a very low elongation at break of 5 %. The material breaks after yield without necking. The addition of NR in the PLA matrix changed the brittle fracture of PLA to a ductile fracture with formation and propagation of a neck while stretching and the yield fracture was suppressed. The addition of the rubber particles significantly lowered the yield stress, arising from softening and formed voids.

It is very interesting to note that a drastic increase of the elongation at break to 200 % is obtained with the addition of 10 wt% of NR. We can conclude that, in this particular case, interfacial adhesion between the PLA and NR phases is not a key factor to improve mechanical properties as we observed low interaction between the two phases. **Figure 12** shows the fractured sections along the tensile direction for PLA and PLA/NR blend 10 wt% after stretching. PLA breaks at very low elongations and the fracture surface is very smooth. The deformation mechanism of PLA has already been studied. Ito et al. demonstrated that on the uniaxial tensile deformation, both shearing deformation and the formation of surface crazes occurred simultaneously with plastic deformation [53]. However, the addition of the

rubber leads to a large plastic deformation with formation of a neck. This result suggests that NR behaves as a stress concentrator and the debonding in the initial stage of stretching occurs at the particle-matrix interface due to the poor interfacial adhesion. This results in the formation of a yield point at which stable plastic deformation takes place. After the yield point, a typical neck starts to form and then extends in a “cold drawing” process driven by the local heating of the specimen due to energy released during deformation. In addition, the material undergoes some whitening in the necked zone, which reflects a fine-scale cavitation process. The un-deformed material contains cavities due to the poor adhesion between PLA and NR, which were clearly increased during the material deformation.

Thus the release of the strain constraint due to the formation of voids and the decrease of yield stress resulted in the relaxation of stress concentration, and in the significant increase of the toughness of the material. Further details of the deformation mechanisms of the samples are currently under consideration and will be reported in the future.

The concentration of 10 wt% of NR seemed to be optimal since a further increase of the rubber content in the blend decreased the elasticity to approximately 70 %. As expected, Young’s modulus and tensile strength of the blends decrease with the addition of NR.

To understand the results of the mechanical properties of PLA/NR 20 wt%, we analysed the ESEM micrographs of the blend before and after compression-moulding as this processing step was used to prepare the samples for mechanical properties (**Figure 13**). We observed a dramatic increase of the average droplet sizes and a broader size distribution due to the coalescence of NR droplets during compression-moulding. This behaviour has been reported for other polymer blends and demonstrates that coalescence of dispersed phase in immiscible blends is not prevented by the high viscosity of polymers [35, 54]. Hence, the coalescence of the NR particles in PLA/NR 20 wt% blends during compression-moulding increased so much the droplet size that the toughening of PLA by NR became ineffective. This coalescence

effect occurred in less proportion for PLA/NR 5 wt% and PLA/NR 10 wt% due to the lower concentration of NR in these blends and thus did not affect PLA/NR 5 wt% and PLA/NR 10 wt% mechanical properties.

4. Conclusions

The addition of natural rubber allows straightforward production of ductile PLA, using a simple blending followed by a compression-moulding technique. The optimal NR content to improve the brittleness of PLA was found to be 10 wt%; at this concentration the rubber droplets provided an optimum balance between their coalescence and their enhancement of both the polymer chain mobility and the material's physical and mechanical behaviour. Tensile testing of the optimal sample showed a drastic increase in the elongation at break from 5 % to 200 % without sacrificing the transparency of the material. Moreover, the small molecules contained in the elastomeric phase could be acting as nucleating agent favouring the crystallisation ability of PLA. The study confirms PLA/NR blends as a viable material to overcome the two main drawbacks of PLA for its use in the packaging sector. Further research will be carried out to reduce the interfacial tension between both polymer phases and to analyse the biodegradation of the materials.

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Figure captions

Figure 1. Morphology and distribution of NR droplets in the PLA/NR blends for different processing temperatures a) 160 °C, b) 180 °C, and c) 200 °C.

Figure 2. Photos taken by optical polarised microscope. Isothermal crystallisation (cooled from 180 °C to 130 °C) of pristine PLA at a) 0 min, b) 30 min, c) 1 h, d) 2 h and processed PLA at e) 0 min, f) 10 min, g) 15 min, and h) 1 h.

Figure 3. Evolution of torque during blending in the twin screw extruder for PLA and PLA/NR 10 wt%.

Figure 4. Mass spectra of the acetone in which the blend was immersed at retention times of 5.9, 6.5, 8.2 and 8.5 min.

Figure 5. Photographs of films of about 150 µm for a) PLA and b) PLA/NR blend at 10 wt%.

Figure 6. Morphology and distribution of rubber droplet size in PLA/NR blends at different NR concentrations a) 5 wt%, b) 10 wt% and c) 20 wt%.

Figure 7. Melting curves of PLA/NR blends.

Figure 8. Evolution of complex viscosity during isothermal crystallisation

Figure 9. Melting curves of crystallised PLA/NR blends

Figure 10. Rheological properties of the PLA/NR blends a) $G'(\omega)$, b) $G''(\omega)$, c) $\eta^*(\omega)$, d) Cole-Cole diagrams.

Figure 11. Average curves of the mechanical properties of the PLA/NR blends.

Figure 12. Fractured surface of stretched materials a) PLA, b) PLA/NR 10 wt%.

Figure 13. Comparison of PLA/NR 20 wt% blend morphology before and after compression-moulding.

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Table 1. Average droplet size of NR in the blend as a function of processing variables and NR concentration

Variables				Average droplet size, μm
Temperature, $^{\circ}\text{C}$	Rotor speed, rpm	Blending time, min	NR concentration, wt%	
160	60	15	10	1.15 ± 0.40
180	60	15	10	2.30 ± 0.70
200	60	15	10	2.30 ± 0.90
160	30	15	10	1.20 ± 0.40
160	90	15	10	1.25 ± 0.40
160	60	10	10	1.15 ± 0.35
160	60	15	5	1.20 ± 0.40
160	60	15	20	2.00 ± 0.70

Table 2. Thermal properties of PLA/NR blends.

	$T_{g, \text{NR}}$ $^{\circ}\text{C}$	$T_{g, \text{PLA}}$ $^{\circ}\text{C}$	T_c $^{\circ}\text{C}$	ΔH_c J/g	T_f $^{\circ}\text{C}$	ΔH_f J/g
Pristine PLA	-	58.4	-	-	-	-
Processed PLA	-	59.6	-	-	150.0	0.13
PLA/NR 5 wt%	-	59.2	-	-	151.2	0.38
PLA/NR 10 wt%	-73.0	57.7	127.6	-9.66	151.0	9.94
PLA/NR 20 wt%	-72.8	59.4	123.5	-17.05	151.3	20.35

Table 3. Thermal properties of PLA/NR blends after crystallisation.

	T_m $^{\circ}\text{C}$	ΔH_m J/g
Processed PLA	152.8	23.57
PLA/NR 5 wt%	151.5	24.82
PLA/NR 10 wt%	150.6	25.20
PLA/NR 20 wt%	150.3	25.46

Table 4. Mechanical properties of PLA/NR blends.

	Young's modulus, GPa	Elongation at break, %	Tensile strength, MPa
Pristine PLA	2.9 ± 0.1	3.3 ± 0.4	63.1 ± 1.1
Processed PLA	3.1 ± 0.04	5.3 ± 0.7	58.0 ± 1.5
PLA/NR 5 wt%	2.5 ± 0.06	48 ± 22	50.4 ± 1.6
PLA/NR 10 wt%	2.0 ± 0.05	200 ± 14	40.1 ± 1.5
PLA/NR 20 wt%	1.8 ± 0.08	73 ± 45	24.9 ± 0.9