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Poly(Lactic Acid)/Natural Rubber Blends

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Abstract. Nowadays biopolymers are in the focus of many research and Poly(lactic acid) (PLA) is the one of the candidates of this field. The rigid behavior of PLA limits its application field, thus it is mostly used for rigid packing. Our research aim is to increase PLA ductility while keeping the biodegradability as much as possible. In our study, PLA was melt mixed in an internal mixer with 5, 10, 20 and 30 wt% natural rubber. It was possible to increase the toughness to a three time higher value compared to neat PLA while the tensile and flexural properties only decreased maximum 30%.

Introduction

Nowadays, the renewable resource-based biopolymers are gaining more and more attention. These biopolymers could provide adequate alternatives to petroleum based polymers in the future. The most prominent representative of this group is the Poly(lactic acid) (PLA), which has good mechanical, optical properties and UV resistance. It could be processed with the conventional thermoplastics technologies. However, the main disadvantage is the rigid behavior of PLA. To increase the toughness of PLA there are several possibilities. One of them is mixing with natural rubber (NR), which keeps the biodegradability of PLA. To increase the PLA toughness with NR, three main criteria must be met: small NR droplets (1-5 μm), homogeneous distribution of the NR, and good interfacial adhesion [1-5]. Another way to increase toughness of PLA is the dynamic vulcanization [6-8]. In this method crosslinking agent was added to PLA/NR blend during the mixing which results in small vulcanized NR droplets dispersed in PLA. In our study we investigated the effect of the natural rubber content and dynamic vulcanization on the properties of PLA and analyzing the connection between the structure and properties were analyzed.

Experimental

For the tests Natureworks 3052D Poly(lactic acid) and bulk natural rubber with a Mooney viscosity ML(1+4)=60-70 were used. Before blend preparations, the PLA was dried for 4 hours. Brabender Plastograph internal mixer was used for making different PLA/NR blends with 5, 10, 20 and 30 wt% NR content and also vulcanized versions were made with 2 phr sulfur, 5 phr zink-oxide, 2 phr stearin acid and 1,5 phr CBS (N-Cyclohexil-2-benztiazil-sulfenamid). The mixing temperature was 190°C and mixing time was 5+5 minutes. The specimens were prepared by hot pressing at 190°C for 5 minutes by applying 15 bars. Tensile, flexural and Charpy impact tests, were carried out to analyze the effect of NR on the mechanical properties of PLA. Also scanning electron microscopy (SEM) and differential scanning calorimetry (DSC) were performed to examine the morphology and crystallinity.

Results and discussion

Our study begun by examining of the toughening effect of NR on the PLA. Unnotched and notched Charpy impact tests were carried out. It was found that the optimum natural rubber concentration is about 5-10 wt%. It can be seen in Fig. 1. that the unnotched impact strength increased from 20.5 kJ/m^2 to 61.3 kJ/m^2 with 10 wt% NR. In the case of notched Charpy tests the best results also could be reached by adding 10 wt% NR to PLA. The unnotched impact strength increased from 3.8 kJ/m^2 to 9.3 kJ/m^2. Over 10 wt% NR the impact energy decreased, also the dynamically vulcanized blends have performed worse.

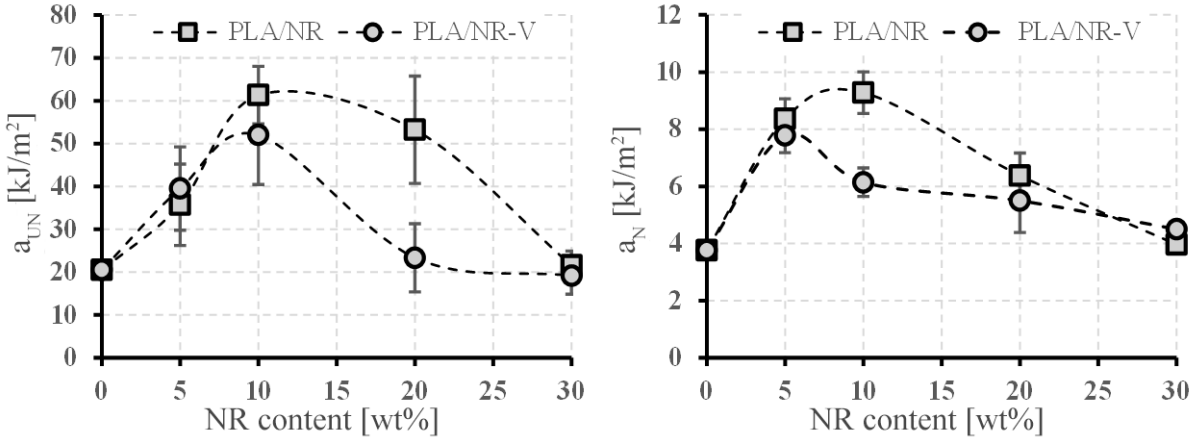


Figure 1. Charpy impact strength of PLA/NR blends: unnotched (a), notched (b)

The blends structure were analyzed with scanning electron microscopy (SEM) and the result can be seen in Fig. 2. The size of NR droplets increased with increasing rubber content and the dispersion were found to be better at lower contents because at higher NR content the shear rate of the internal mixer was not enough to disperse the NR correctly in the PLA matrix. Connected to the Charpy measurements, it was found that the impact strength were significantly affected by the NR droplets size and distribution. The critical value in diameter was about 5 μm, above this value negative effect was observed. It is visible that the level of adhesion between the PLA and NR is quiet low, surface treatment needed for in further research.

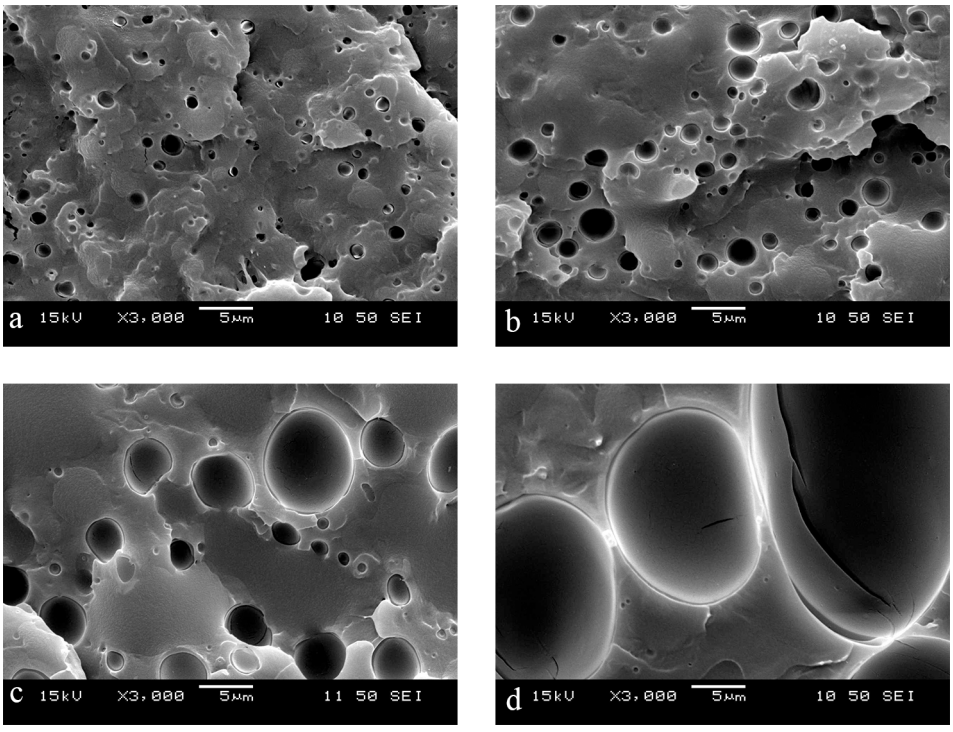
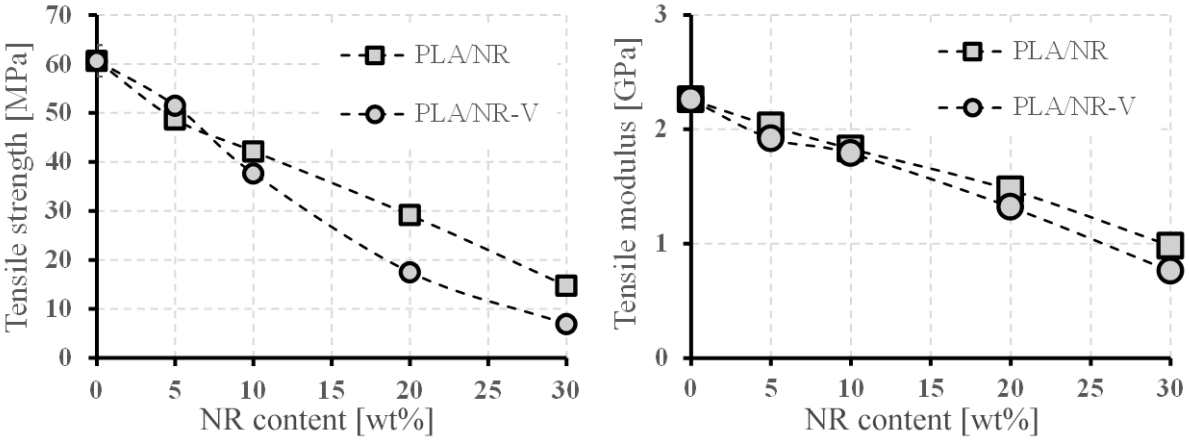


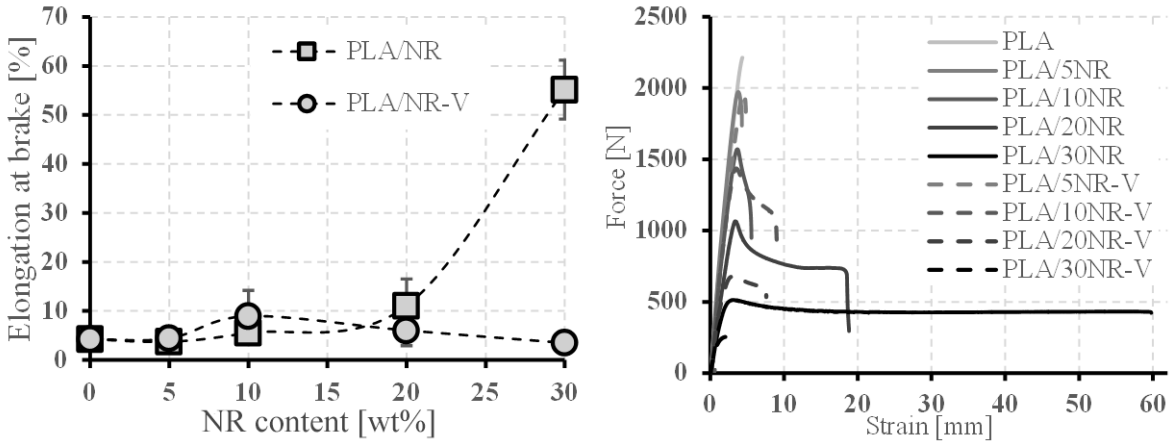
Figure 2. SEM images of PLA/NR blends: 5 wt% (a), 10 wt% (b), 20 wt% (c), 30 wt%(d)

Tensile and flexural properties were also investigated in a function of NR content. By adding 10 wt% of NR the impact strength increased up to 61.3 kJ/m^2 while both the tensile strength and modulus decreased linearly to 42 MPa and 1,8 GPa (Fig. 3.), but it is quite enough for average applications made by polypropylene (PP) or acrylonitrile-butadiene-styrene (ABS). The properties of vulcanized blends decreased more than the non-vulcanized. The NR had significant effect on the elongation at brake over 20 wt% (12%) and it is increased up to 55% with 30% NR. In the case of vulcanized compounds no major changes were seen (Fig. 4.).



a b

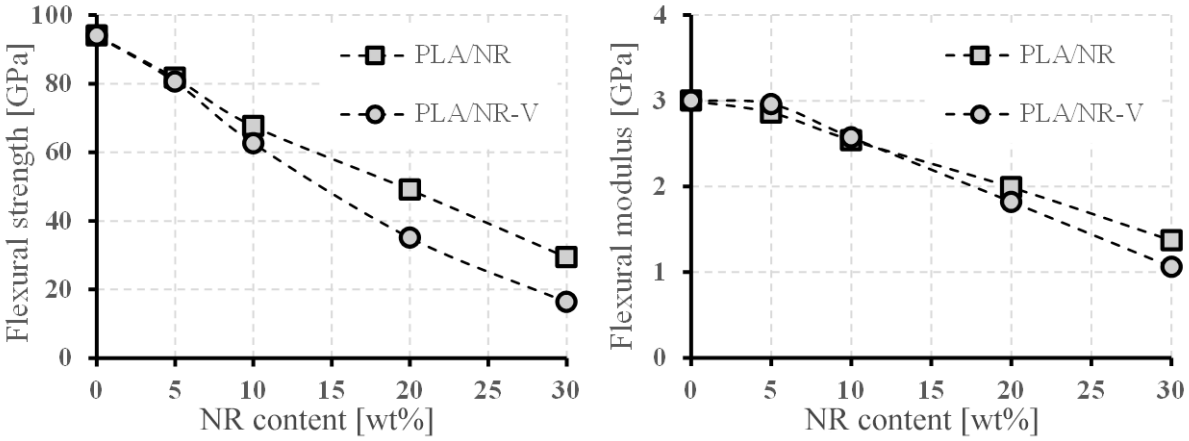
Figure 3. Tensile properties of PLA/NR blends: tensile strength (a), tensile modulus (b)



a b

Figure 4. PLA/NR blends elongation at brake (a), and tensile characteristics (b)

The flexural properties of the blends were also measured, the results can be seen in Fig 5. It shows the same tendency as for the tensile properties. The flexural strength and modulus linearly decreased with increasing NR content. The optimum NC content was found – from the point of view of impact strength – when the flexural strength is 70% of the reference which is 67 MPa, and the modulus is 85% of the reference. Also at higher NR contents the vulcanized blends had worse results.



a b

Figure 5. Flexural properties of PLA/NR blends: flexural strength (a), flexural modulus (b)

The crystallinity (X_c) and the glass transition temperature (T_g) were analyzed with differential scanning calorimetry (DSC) from the first heating scan (2°C/min 0-200°C). It was found that the natural rubber had no significant effect on both the crystallinity and glass transition temperature (Table 1. and Fig 6).

Table 1. DSC results

	Tg [°C]	Xc [%]
PLA	58.9	2.7
PLA/5NR	57.5	5.4
PLA/10NR	59.9	7.6
PLA/20NR	62.1	4.2
PLA/30NR	58.2	2.4
PLA/5NR-V	60.2	3.6
PLA/10NR-V	61.0	3.7
PLA/20NR-V	55.9	3.4
PLA/30NR-V	55.1	8.5

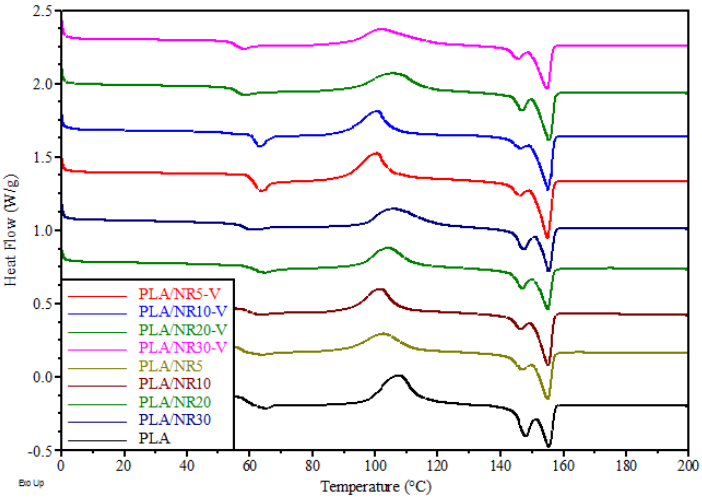


Figure 5. DSC first heating scans

Summary

In our work the effect of the natural rubber (NR) content and dynamic vulcanization on the properties of Poly(lactic acid) (PLA) were analyzed and the connection between structure and properties was examined. The measurements results showed that the optimum NR content is about 10 wt% and by adding this amount to PLA, three time higher Charpy impact strength was found compared to neat PLA at the cost of maximum 30% decrease in both tensile and flexural strength and moduli. Scanning electron microscopy showed that at lower NR contents the dispersion was better and the NR droplets size was under 5 μm, however over 10 wt% bigger NR doplets were found which caused significant decrease in the impact strength. DSC measurements were also carried out but no significant effect was found.

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