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Influence of Ultrasound Parameters on the Mechanical and Rheological Properties of PLA/PBAT Blends Compatibilized with an Epoxy-Based Chain Extender

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Abstract: In this work, 50/50 wt% blends of PLA and PBAT with and without a chain extender agent with multifunctional epoxy groups (Joncryl ADR-4468) were prepared by ultrasound-assisted melt blending in a Brabender chamber. The ultrasound parameters that were analyzed were the time (0, 5, 10, and 15 minutes), the frequency (20±0.5 KHz), and the power (188, 375, 562, and 750 W) applied. The torque rheograms showed an increase in the final torque when increasing the time and power of ultrasound at a constant frequency, mainly in the blends prepared with a chain extender. The complex viscosity of the blends without a chain extender gradually decreased with time and ultrasound power at a constant frequency, while in the blends prepared with a chain extender, an opposite effect was observed; the complex viscosity increased with increasing time and ultrasound power. The compatibilized blends with the chain extender showed increased Young's modulus and elongation at break compared to blends without an extender using the same ultrasound conditions. The previous results indicate that the application of ultrasound favored the compatibility of the immiscible PLA/PBAT blends with the chain extender agent.

Introduction

Aliphatic bio-based polyesters like polylactic acid (PLA) are widely used in various fields of application due to their biodegradability. However, they have disadvantages such as high rigidity and, consequently, increased brittleness. The above explains the efforts to blend them with other synthetic biodegradable polymers with high ductility, such as PBAT (Polybutylene adipate- co-terephthalate). However, these blends are immiscible, leading to phase separation, which limits the enhancement of their physical properties.

In this work we prepared 50/50 wt % blends of PBAT and PLA, blends with and without a chain extender agent with multifunctional epoxy groups (Joncryl ADR-4368) by ultrasound-assisted melt blending with variations in power, time and frequency in order to observe changes in their thermal and rheological behavior, morphology, miscibility and mechanical properties with the effects of ultrasonic radiation in combination with an epoxy based multifunctional chain extender.

Experimental

Materials. PLA (Ingeo Biopolymer 2003D, MFR = 6 g/10 min) was purchased from NatureWorks, and PBAT (Dawenco 0101, MFR = 3.5 g/10 min) was purchased from Dawn Degradable Materials. Joncryl ADR-4468 with an epoxy equivalent weight of 310 g/mol was adquired from BASF Corporation.

Methods. PLA/PBAT blends were prepared in a Brabender chamber with a composition of 50/50 wt% at a temperature of 190 °C. The blends with chain extender included it with a 0.5 wt%. The application of ultrasound irradation was performed with a home-made equipment coupled to the mixer chamber (see Figure 1). The ultrasound parameters that were analyzed were the time (0, 5, 10, and 15 minutes), the frequency (20±0.5 KHz), and the intensity of power (25, 50, 75, and 100%) applied. Capillary and oscillatory rheometry also occur at 190 °C, covering shear rates from 30 to 6,000 s^{-1}.

Figure 1. Torque Rheometer equiped with an ultrasonic equipment: sonotrode, generator and converter.

Results y Discussion.

Melt blending assisted with ultrasound radiation. Figures 2 and 3 shows the bar charts of the final torque of the blends, with and without the chain extender, according with the variations in time and power respectively compared with a blend prepared without ultrasound radiation. In the blends without the chain extender the final torque rises as the time of ultrasound increases to 10 minutes and then it doesn't change anymore, whereas in the blend with chain extender the final torque is elevated as the ultrasound time increases.

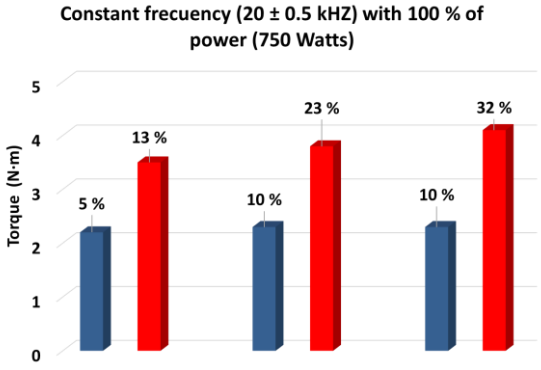


Figure 2. Final torque values vs time (min)

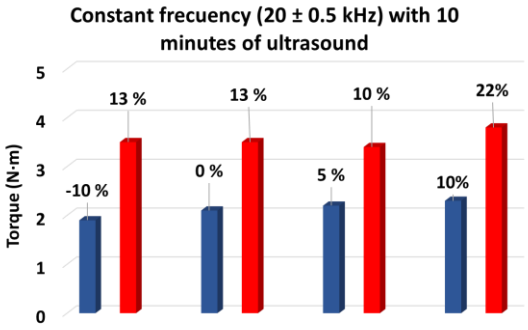
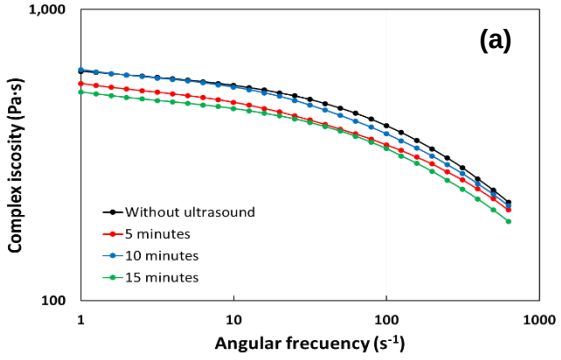


Figure 3. Final torque values vs power (%)

In Fig. 3 the final torque of blends with and without extender is higher as the percent of power increases, but this increase is higher in the blends with a chain extender

Dynamic rheological measurements. Dynamic oscillatory experiments were performed to correlate the torque results with the complex viscosity of the blends. Figure 4 shows the oscillatory rheological behavior of PLA/PBAT blends with ultrasound time, whereas Figure 5 shows the oscillatory rheological behavior of PLA/PBAT blends with power intensity.

Blends without chain extender showed a decrease in their complex viscosities with time and power of ultrasound radiation, but the blends with chain extender had an opposite effect, their complex viscosities increase with time and power.



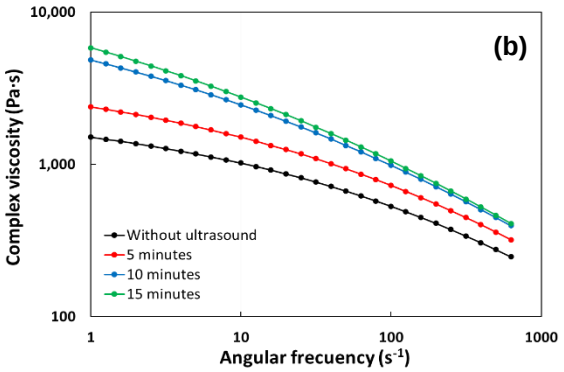


Figure 4. Effect of time on complex viscosity curves vs frequency (a) without chain extender, (b) with chain extender.

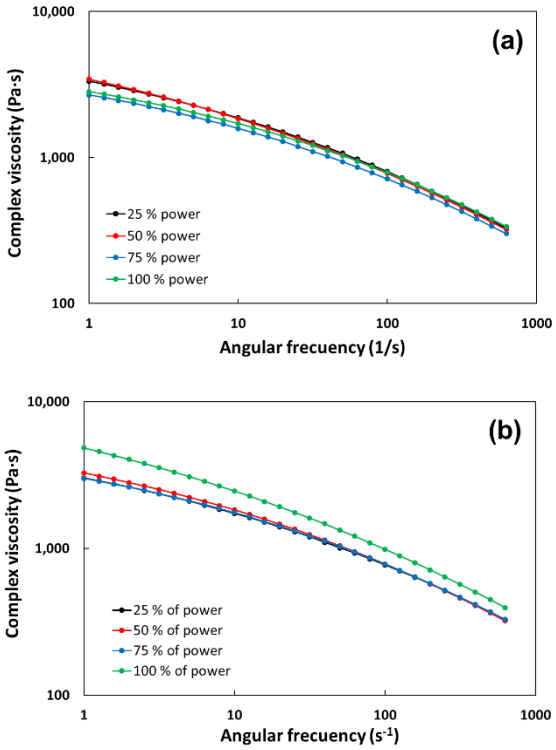


Figure 5. Effect of power intensity on complex viscosity curves vs frequency (a) without chain extender, (b) with chain extender

These results indicate that ultrasound radiation favored the reaction of PLA/PBAT

Figure 6 shows the storage and loss modulus curves of the blends with and without the chain extender.

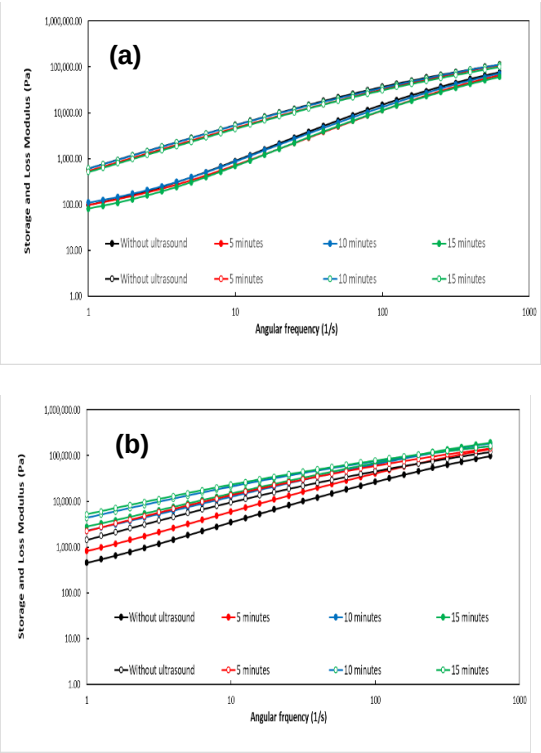
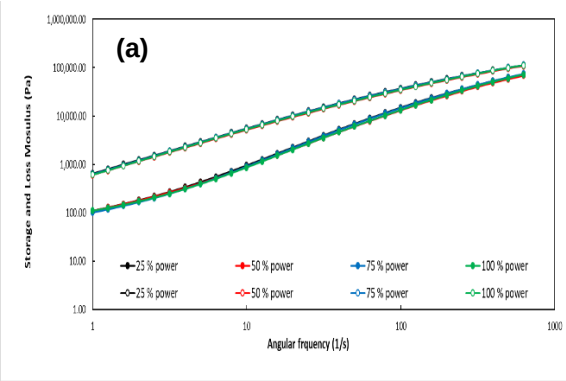


Figure 6. Effect of time on storage and loss modulus curves vs frequency (a) without chain extender, (b) with chain extender.

The reaction of compatibilization of PLA/PBAT blends with a chain extender produced an increase in the loss and storage moduli in the frequency range analyzed, compared with the blends prepared without the chain extender.

In the blends without a chain extender the storage and loss moduli presented similar values but in the blends with chain extender these moduli increased with the time of application of the ultrasound radiation.

Figure 7 shows the effect of the intensity of power in the viscoelastic behavior of the PLA/PBAT blends.



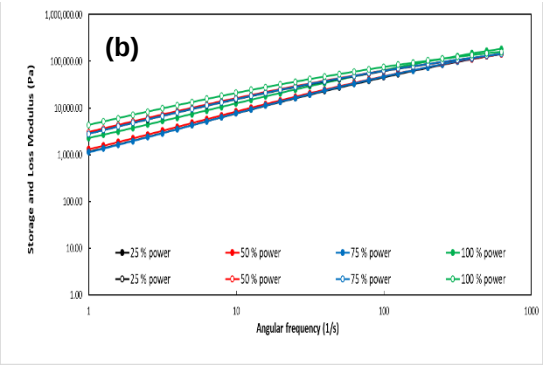


Figure 7. Effect of power intensity on storage and loss modulus curves vs frequency (a) without chain extender, (b) with chain extender.

As in Figure 6, the loss and storage moduli of the blends without chain extender remains without a significant change, but the blends with the chain extender presented an increase in loss and storage moduli with the power intensity as a result of the increased viscosity of the blends.

The values of the zero shear viscosity and the modulus in the crossover point are summarized in Tables 2 an 3.

Table 2. Effect of time in the mechanical properties of PLA/PBAT blends.

Sample	Time (min)	Zero Viscosity (Pa·s)	Cross modulus (Gx) (Pa)
PLA/PBAT	0	631.71	-
	5	627.5	-
	10	662.92	-
	15	536.75	-
PLA/PBAT/CE	0	2351.2	-
	5	4407.0	-
	10	20416.0	1.13E+05
	15	35321.0	1.04E+05

Table 3. Effect of power intensity

Sample	Power (%)	Zero Viscosity (Pa·s)	Cross modulus (Gx) (Pa)
PLA/PBAT	25	684.7	-
	50	651.3	-
	75	662.58	-
	100	662.92	-
PLA/PBAT/CE	25	7664.6	1.44E+05
	50	8606.8	1.36E+05
	75	6951.2	1.37E+05
	100	20416.0	1.13E+05

In these results we observed that the blends without chain extender had a slight increase in the zero shear viscosity with time and power, but the blends with chain extender presented a notorious increase in the zero shear viscosity with time and principally with the intensity of power.

Mechanical properties. Tensile properties of PLA/PBAT blends are shown in Table 1. These properties improved with time and power of ultrasound radiation, especially the blends prepared with a chain extender.

Table 1. Tensile properties of PLA/PBAT blends

Sample	Time (min)	Young Modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
PLA/PBAT	0	260 ± 5.6	13.15 ± 0.1	3.09 ± 1.8
	5	366 ± 5.9	16.64 ± 1.1	3.59 ± 2.2
	10	336 ± 15.9	15.55 ± 0.5	3.05 ± 1.8
	15	322 ± 11.7	15.31 ± 0.8	3.31 ± 2.0
PLA/PBAT/CE	0	319 ± 3.4	15.53 ± 0.7	5.07 ± 3.3
	5	343 ± 12.6	18.90 ± 0.7	38.48 ± 24.1
	10	348 ± 20.7	19.02 ± 0.7	17.99 ± 12.1
	15	3501 ± 0.8	20.65 ± 3.5	84.71 ± 66.8

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PLA/PBAT/CE	0	319 ± 3.4	15.53 ± 0.7	5.07 ± 3.3
	5	343 ± 12.6	18.90 ± 0.7	38.48 ± 24.1
	10	348 ± 20.7	19.02 ± 0.7	17.99 ± 12.1
	15	3501 ± 0.8	20.65 ± 3.5	84.71 ± 66.8

Conclusions.

According with these results the best conditions are 100 % power and longer time of the ultrasound during the melt blending (10 to 15 min). The time and the power used of the ultrasound radiation produced changes in the viscosity and mechanical properties, making the material have a ductile or brittle behavior according the time and the power of the ultrasound radiation.

Acknowledgements

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