

Natural Rubber-Toughened PHBV/PLA Bioplastic Films for Quieter Packaging Applications

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Presented at the Fall 196th Technical

Meeting of Rubber Division, ACS

Cleveland, OH

October 8-10,

2019

ISSN: 1547-1977

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ABSTRACT

Bio-based and industrially compostable plastic films from polylactide (PLA) and blends of PLA, natural rubber (NR), and poly-(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) were prepared through casting. Addition of NR and PHBV altered PLA physical, mechanical, and thermal properties. NR addition improved PLA flexibility, decreased PLA crystallinity, increased PLA onset degradation temperature and dampened the sound produced by PLA film deformation, with 15% rubber loading resulting in partial miscibility between PLA and NR. PHBV addition also improved PLA flexibility, decreased PLA glass transition temperature, onset and peak degradation temperatures, and degree of crystallinity, with 20% PHBV loading resulting in the most significant increase in PLA tensile strain. Addition of both NR (15%) and PHBV (17%) significantly decreased PLA storage modulus and noise. The films from PLA, NR, and/or PHBV blends with a variety of physical and mechanical performance properties can potentially be used for packaging applications especially where quieter or silent biodegradable plastic bags are needed.

INTRODUCTION

Plastic films account for 35% of the packaging market¹. They exhibit the fastest growth in demand, driven by the expanding popularity of pouches for a variety of food items, as well as the rise in active and intelligent packaging². Conventional plastics, which are petroleum-based and non-biodegradable, are the dominant film resins, and the packaging industry is looking for bio-based alternatives to attain environmental sustainability. Currently, the most commonly used bio-plastics are starch blends, Bio-PET, and polylactide (PLA) and PLA blends³. However, significant issues impede their use as food packaging films: starch blends are moisture sensitive, Bio-PET is not biodegradable, and PLA is brittle and rigid, and deforms at low temperature⁴.

Polyhydroxyalkanoates (PHAs) are a group of promising polyesters produced through bacterial fermentation of renewable sugar and lipid resources⁵. They are biodegradable in a natural environment and take only two months to decompose in backyards⁶. These polymers possess low moisture permeability like low-density polyethylene (LDPE) and mechanical properties similar to polypropylene (PP) as well as high heat deflection temperature. However, PHAs are stiff and brittle, limiting their applications in the packaging industry. Incorporation of poly-(3-hydroxyvalerate) into PHB can improve its toughness and poly-(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) has improved potential as a food packaging material⁷.

In previous research, the flexibility and toughness of PHBV were improved by incorporation of natural rubber (NR)⁸⁻¹⁰. NR particles dispersed in the plastic matrix act as stress concentrators and improve the toughness of the plastic by absorbing energy through yielding and cavitation. NR can also disperse heat more efficiently than thermoplastics, leading to improved thermal stability of the plastic matrix. As NR is less dense than PHBV, the addition of rubber can also improve the yield of PHBV-based products. PHBV and NR blends were successfully made into food trays which tolerated acidic food well. Therefore, the goal of this study was to explore the possibility of improving the flexibility and toughness of PHA, PHBV and PLA films with the addition of natural rubber. The effect of rubber on noise reduction of the bio-films was also evaluated.

MATERIALS AND METHODS

BIOPLASTIC FILM PREPARATION

A variety of bioplastic films made from pristine PLA (purchased from NatureWorks, Minnetonka, MN), PLA/PHBV (purchased from Sigma-Aldrich, St. Louis, MO, contains 8% HV), PLA/NR (purchased from Centrotech Rubber Inc., Chesapeake, VA), and PLA/PHBV/NR blends were prepared by casting with chloroform at 60 °C (TABLE I). The prepared film samples were dried at ambient temperature for two weeks before testing.

TABLE I
COMPOSITIONS OF BIOPLASTIC FILM SAMPLES

Samples	PLA (wt. %)	PHBV (wt. %)	NR (wt. %)
PLA	100	0	0
PLA/NR (90/10)	90	0	10
PLA/NR (85/15)	85	0	15
PLA/NR (80/20)	80	0	20
PLA/PHBV (90/10)	90	10	0
PLA/PHBV (80/20)	80	20	0
PLA/PHBV (70/30)	70	30	0
PLA/PHBV/NR (72/18/10)	72	18	10
PLA/PHBV/NR (68/17/15)	68	17	15
PLA/PHBV/NR (64/16/20)	64	16	20

MECHANICAL CHARACTERIZATION

Tensile strength and tensile elongation at break of the film samples were measured by an Instron 5542 equipped with a Bluehill v. 2.17 software package (Instron Corp. Norwood, MA) according to ASTM D882-12. The testing was conducted at a crosshead speed of 50 mm/min and an initial gap separation of 50.8 mm with five replicates. Storage and loss moduli of the film samples (18.00 x 7.00 x 0.05 mm³) were measured using a TA Instrument Q800 Dynamic Mechanical Analysis (DMA) instrument (TA Instruments, New Castle, DE) equipped with tension clamps. The samples were tested at a sinusoidal deformation of 15 μ m and a frequency of 1 Hz with a preload force of 0.01 N. The samples were rapidly cooled to -30 °C and held isothermally for 5 minutes, and then heated to 160 °C at a rate of 5 °C /min.

THERMAL ANALYSIS

Melting and glass transitions of the film samples were characterized using a TA Differential scanning calorimetry instrument (DSC2500, TA Instruments, New Castle, DE). The samples were heated from -20 to 200°C at a rate of 10°C/min, held there isothermally for 5 min, cooled to -85°C at 10 °C/min, isothermally held for 5 min, and reheated to 200 °C at 10 °C/min. Thermogravimetric analysis of the film samples were conducted using a TGA550 (TA Instruments, New Castle, DE) from room temperature to 500 °C at 20 °C /min.

RHEOLOGICAL CHARACTERIZATION

Complex viscosities of the materials were analyzed using a TA Instrument Ares LSII rheometer (New Castle, DE, USA), to explore the feasibility of melt blending PLA with PHBV and/or NR for film blowing. Rheological determinations were performed at 175 C using a 25 mm parallel plate system. Each disk sample, with a thickness of 1 mm and diameter of 25 mm, was equilibrated for 5 min before the gap was set to the testing position of approximately 0.9 mm or

until the top plate made contact with the upper surface of the sample. The complex viscosity was measured with increasing frequency from 0.1 to 100 rad/s at a 0.3% strain.

SOUND LEVEL TEST

The noise made by the film samples under physical manipulation was tested in a sound proof studio equipped with audio amplification testing software in Garageband 10.2.0 (Apple, Cupertino, CA) and an Audio-Technica Auray TT-6240 USB microphone.

RESULTS AND DISCUSSION

FILM APPEARANCE

The films from pristine PLA and blends from PLA, PHBV, and NR blends consistently had good transparency (Fig. 1). The transparency of the films is an attractive trait that is vital to the selection of a truly optimal product. Film from PLA/PHBV/NR blends appeared cloudy in the middle (Fig. 1D), caused by the incompatibility between rubber and PLA/PHBV bioplastics.

A that material specification before using this test Table 1 in Classification D4000 lists the ASTM standards that currently exist.

The tensile properties can be utilized to provide data for research and development and engineering design as well as quality control and specification. However, data from such tests cannot be considered significant for applications differing widely from the load-time scale of the test employed.

3 The tensile modulus of elasticity is an index of the stiffness of thin plastic sheeting. The reproducibility of test results is good when precise control is maintained over all test conditions. When different materials are being compared for tensile properties, specimens of identical dimensions must be employed.

The tensile energy to break (TEB) is the total energy absorbed per unit volume of the specimen up to the point of fracture. In some texts this property has been referred to as impact energy. It is used to evaluate materials that are subjected to impact or that can stall web transport equipment in the operation of a machine malfunction in end-use applications. Factors such as the rate of strain, specimen parameters, and especially the rate of strain, specimen parameters, and especially the rate of strain can cause large variations in the results. In that

B tip is used, care must be taken to ensure that the test specimen is inserted and clamped so that the long axis of the test specimen coincides with the direction of pull through the center line of the grip assembly.

5.1.3.2 Self-aligning grips are attached to the fixed and movable members of the testing machine in such a manner that they will move freely into alignment as soon as a load is applied so that the long axis of the test specimen will coincide with the direction of the applied pull through the center line of the grip assembly. The specimens must be aligned as perfectly as possible with the direction of pull so that no rotary motion will cause slippage to occur in the grips; there is a limit to the amount of misalignment self-aligning grips will accommodate.

5.1.3.3 The test specimen shall be held in such a way that slippage relative to the grips is prevented insofar as possible. Grips lined with thin rubber, crocus-cloth, emery cloth, or pressure-sensitive tape as well as file-faced or serrated grips have been successfully used for many materials. The choice of grip surface will depend on the material tested, thickness, etc. Line grips padded on the round face with 0.75-1.00 mm (0.030-0.040 in.) blotting paper or filter paper have been found

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D center line of the grip assembly. The direction of pull through the

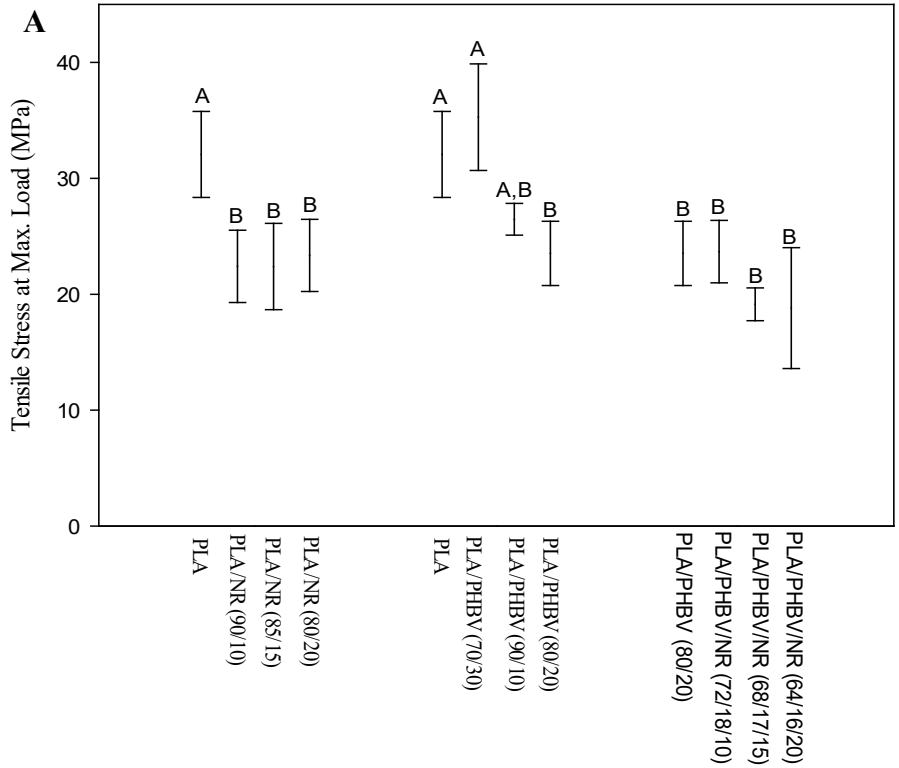
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Fig. 1. The appearance of film samples: (A) pristine PLA, (B) PLA/NR blend (85/15), (C) PLA/PHBV blend (80/20), (D) PLA/PHBV/NR blend (68/17/15)

MECHANICAL PROPERTIES

Addition of PHBV and NR decreased PLA strength (Fig. 2A), but increased PLA tensile elongation (Fig. 2B) as they have higher flexibility than PLA. Addition of 20% PHBV resulting in the greatest increase in PLA tensile strain.



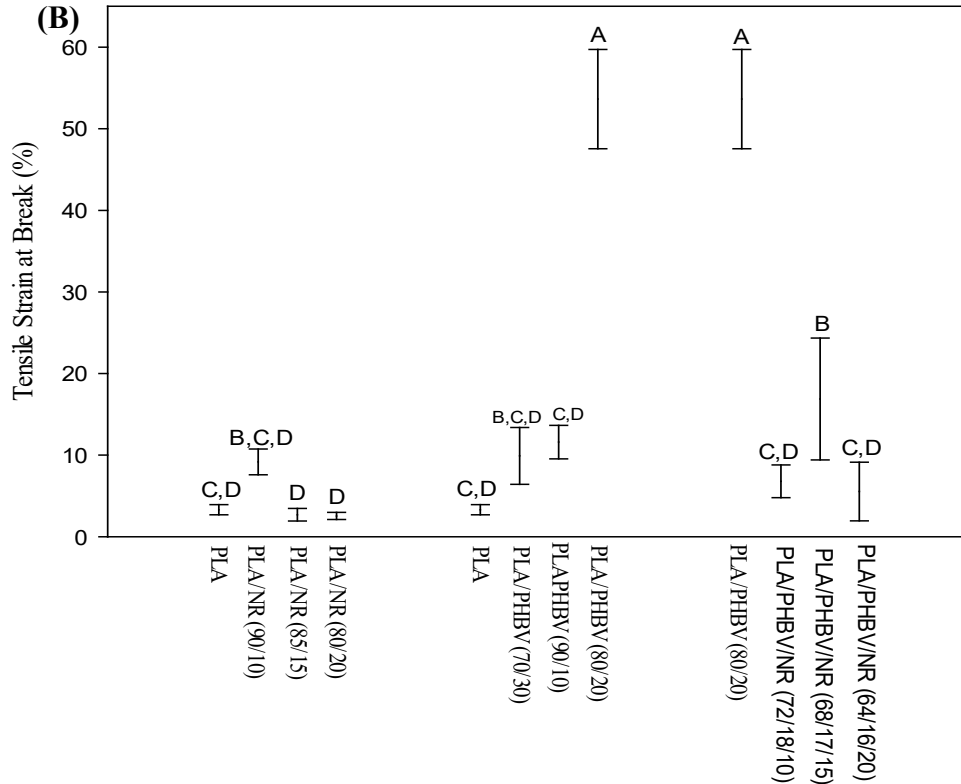


Fig. 2. Tensile stress (A) and tensile strain (B) at break of film samples from PLA and blends of PLA/PHBV, PLA/NR, and PLA/PHBV/NR. Different letters denote statistical difference at $P > 0.05$

Additions of NR and PHBV impacted PLA storage modulus (Fig. 3A). Addition of 15% NR decreased PLA storage modulus, due to NR's softness and low storage modulus, also indicating partial miscibility between NR and PLA. Interestingly, higher (20%) or lower (10%) rubber content in PLA/NR blends had minimal effect on PLA storage modulus, which may be caused by the incompatibility between NR and PLA. This result indicates that a 15% NR loading provides optimal miscibility between PLA and NR without addition of any compatibilizers. Addition of PHBV also decreased PLA storage modulus (Fig. 3B). The most noticeable change in PLA storage modulus was observed when both NR and PHBV were added, with addition of 15% NR and 17% PHBV resulting in the greatest decrease of PLA storage modulus (Fig. 3C).

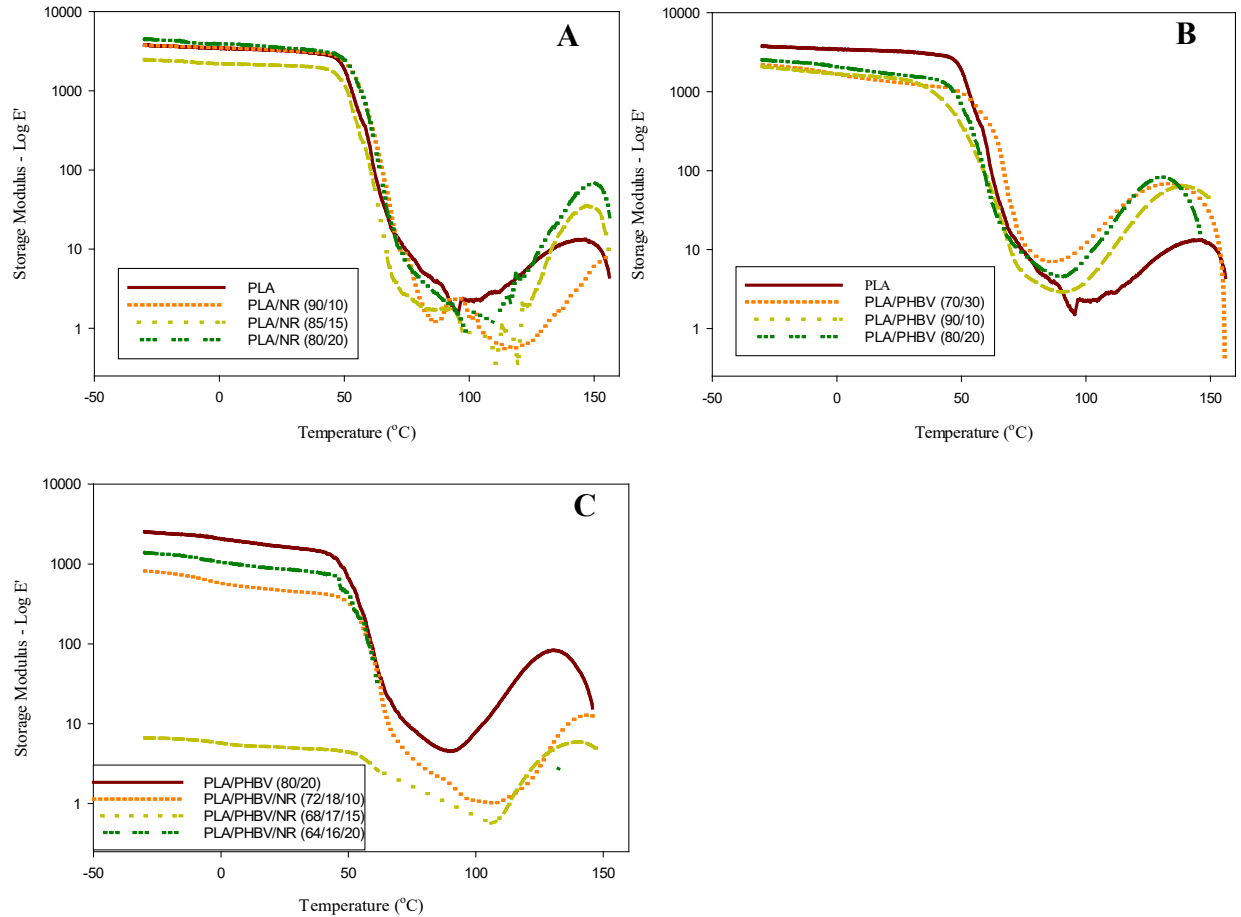


Fig. 3. Storage modulus of films samples from PLA, PLA/NR blends (A), PLA/PHBV blends (B), and PLA/PHBV/NR blends (C)

THERMAL PROPERTIES

The melting temperatures of the PLA/NR blends (149-151 °C) resembled that of native PLA (149 °C), with T_m slightly decreasing with increasing rubber loadings (TABLE II). Addition of 10-20% PHBV slightly increased PLA melting temperature while addition of 30% PHBV decreased PLA melting temperature. Addition of both NR and PHBV increased PLA T_m by 2 °C. NR alone had no effect on PLA glass transition in the blends, while addition of PHBV alone or with NR decreased PLA glass transition temperature by 2.6-4.6 °C, indicating partial compatibility between PHBV and PLA. The decreased blend T_g may contrifer improved flexibility. Addition of NR and 10-20% PHBV decreased PLA crystallinity while addition of 30% PHBV significantly increased this property, indicating that 30% PHBV acted as a nucleating agent in the blend.

TABLE II

MELTING (T_m) AND GLASS TRANSITION (T_g) TEMPERATURES AND DEGREE OF CRYSTALLINITY (ΔC) OF PLA, PLA/NR, PLA/PHBV, AND PHBV/PHBV/NR DETERMINED FROM DSC

Samples	T_m (°C)	T_g (°C)	ΔC (%)
PLA	149.1 ± 0.30	61.9 ± 0.17	16.6
PLA/NR (90/10)	150.2 ± 0.40	61.4 ± 0.35	6.6
PLA/NR (85/15)	149.5 ± 0.08	61.8 ± 0.29	11.9
PLA/NR (80/20)	149.7 ± 0.02	61.7 ± 0.16	8.4
PLA/PHBV (90/10)	150.9 ± 0.46	59.3 ± 0.38	2.8
PLA/PHBV (80/20)	151.3 ± 0.07	59.3 ± 0.63	9.9
PLA/PHBV (70/30)	148.3 ± 0.30	57.3 ± 0.33	34.3
PLA/PHBV/NR (72/18/10)	151.7 ± 0.59	58.3 ± 0.01	6.3
PLA/PHBV/NR (68/17/15)	151.3 ± 0.04	58.5 ± 0.03	3.2
PLA/PHBV/NR (64/16/20)	151.6 ± 0.03	58.5 ± 0.08	3.3

All of the PLA/NR blends had one degradation stage as PLA and NR had consistently similar peak degradation temperatures. The degradation of the blends started at 322-327 °C and peak degradation occurred at 383-384 °C, which is close to PLA's peak degradation temperature (TABLE III). NR addition increased PLA onset degradation temperature by ~ 2-7 °C, due to it having a higher onset degradation temperature than PLA, indicating patricidal miscibility between NR and PLA. NR addition also improved PLA thermal stability.

Unlike the PLA/NR blends, the blends of PLA/PHBV and PLA/PHBV/NR degraded in two stages (TABLE IV), reflecting the different thermal stabilities of PLA and PHBV. The first thermal degradation stage, between 290 and 300 °C, was associated with PHBV degradation, while the second stage, between 372 and 384 °C, indicated PLA and/or NR degradation. Addition of PHBV slightly decreased both PLA and PLA/NR peak degradation temperatures except 20% PHBV loading in the PLA/PHBV blend which had no effect on PLA peak degradation temperature.

TABLE III

ONSET (T_o) AND PEAK (T_p) DEGRADATION TEMPERATURES OF PLA AND PLA/NR BLENDS DETERMINED FROM TGA

Samples	T_o (°C)	T_p (°C)
PLA	319.9 ± 0.83	383.2 ± 1.41
NR	370.0 ± 3.20	394.7 ± 1.16
PLA/NR (90/10)	322.5 ± 0.22	383.6 ± 1.68
PLA/NR (85/15)	327.4 ± 1.17	384.4 ± 0.21
PLA/NR (80/20)	322.2 ± 0.63	382.9 ± 0.01

TABLE IV

ONSET (T_o) AND PEAK (T_p) DEGRADATION TEMPERATURES OF PLA/PHBV AND PLA/PHBV/NR BLENDS DETERMINED FROM TGA

Samples	T_o of PHBV (°C)	T_p of PHBV (°C)	T_o of PLA (°C)	T_p of PLA (°C)
PLA	-	-	319.9 ± 0.83	383.2 ± 1.41
PHBV	293.2 ± 0.20	299.4 ± 0.93	-	-
PLA/PHBV (90/10)	274.5 ± 6.45	299.3 ± 5.23	320.6 ± 2.52	381.8 ± 2.53
PLA/PHBV (80/20)	271.8 ± 0.37	304.1 ± 0.22	328.7 ± 0.45	383.9 ± 1.73
PLA/PHBV (70/30)	263.6 ± 1.37	294.9 ± 0.39	317.9 ± 0.39	374.5 ± 0.40
PLA/PHBV/NR (72/18/10)	266.7 ± 1.03	297.2 ± 0.71	321.0 ± 0.01	377.5 ± 0.57
PLA/PHBV/NR (68/17/15)	258.6 ± 1.51	291.1 ± 3.61	315.4 ± 3.31	374.8 ± 1.49
PLA/PHBV/NR (64/16/20)	265.9 ± 1.22	296.4 ± 0.45	319.4 ± 0.01	372.7 ± 2.48

NOISE TEST RESULTS

NR reduced the noise of PLA films by up to 50% (Fig. 4), with higher rubber loading leading to more significant noise reduction, due to NR's sound wave dampening effect. The addition of PHBV also dampened PLA noise. Addition of 16% PHBV and 20% NR together resulted in the most significant reduction in PLA noise. PLA films with reduced noise are preferred where quieter or silent plastic bags are needed, such as movie theaters.

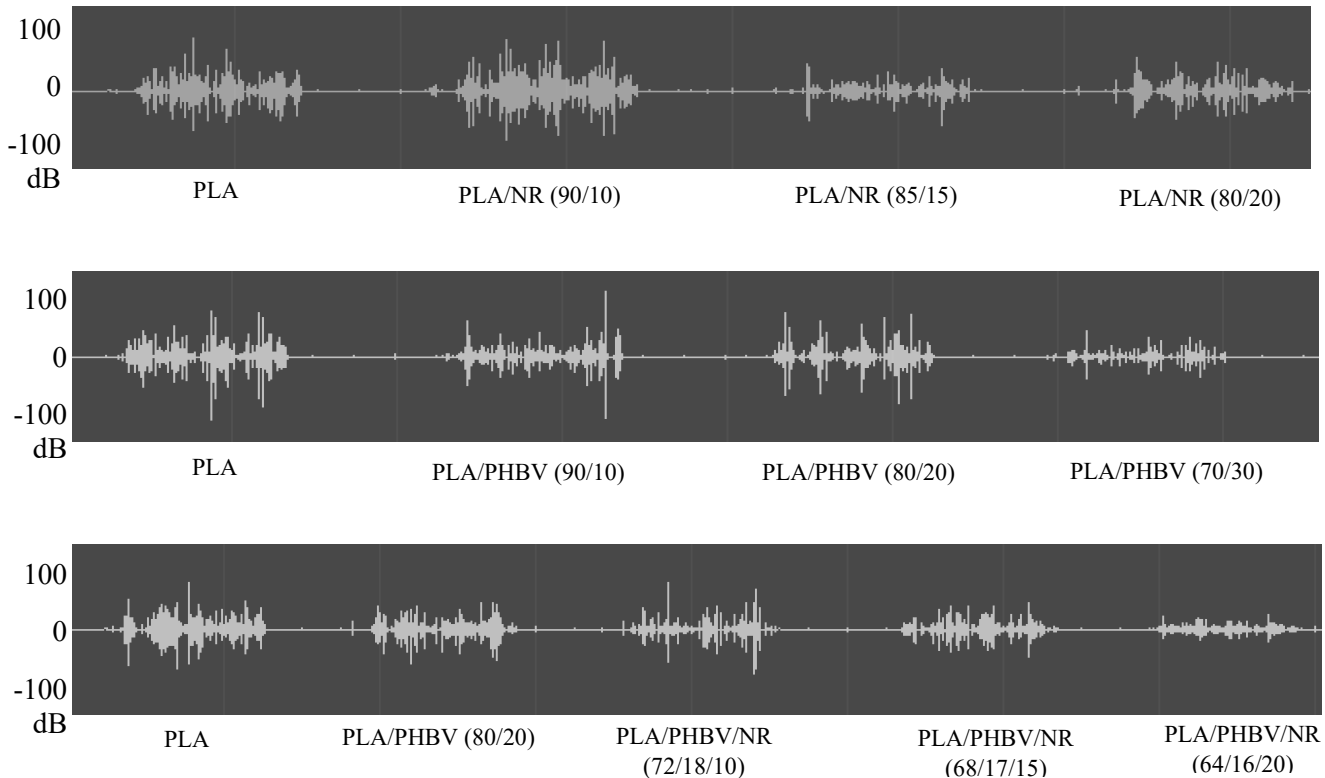


Fig. 4. Audio readings of different film compositions. Y-axis is in decibels as the larger vertical peaks equate to a louder material

CONCLUSIONS

Bio-based and biodegradable plastic films from blends of PLA, NR, and/or PHBV with improved flexibility and thermal stability and reduced noise compared with pristine PLA were successfully produced. The films with a variety of physical and mechanical performance can potentially be used for in a range of packaging applications. Further studies on improving compatibility between PLA, NR, and PHBV are needed to further improve blend performance and develop specific blends matched to individual products.

ACKNOWLEDGEMENTS

This work was supported by the Center for Advanced Processing and Packaging Studies (CAPPS) [grant number: 60065449].

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