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CRADA FINAL REPORT: NITRILE-CONTAINING RENEWABLE POLYMERS BASED ON LIGNIN, (CRADA) NO. NFE 1807437

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Technology Innovation Program

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ABSTRACT

Lignin remains one of the world's largest sources of renewable carbon and has significant potential to reduce carbon emissions by replacing fossil fuel–derived materials, including engineering thermoplastics and their composites. However, efforts to incorporate significant quantities of lignin into engineering thermoplastics as anything other than an inert filler have to date been largely unsuccessful because of limitations imposed by the degradation temperature of the lignin (220°C) and poor compatibility between the lignin and nonpolar or slightly polar polymers.[1] Recent work at the US Department of Energy's Oak Ridge National Laboratory (ORNL) has shown that the right conditions can achieve excellent compatibility between lignin and nitrile-containing rubber compounds such as nitrile butadiene rubber (NBR). The present work extends these findings to the incorporation of lignin into acrylonitrile butadiene styrene (ABS) engineering plastics. Although simple binary mixing of lignin into commercial ABS resins leads to poor interfacial adhesion and resultant low toughness and ductility, appropriately matching the lignin, ABS components, and any appropriate compatibilizing agents leads to polymer blends incorporating 20%–35% by weight lignin with a useful range of mechanical properties for many current ABS applications. By modifying the composition, the balance of properties can be readily tailored to meet the demands of specific end-user applications.

1. BACKGROUND

ORNL demonstrated the ability to control mesoscale morphology in amorphous organic polymer blends consisting of lignin and nitrile rubber.[2] Such control in microstructure helps achieve performance equivalent to thermoplastic elastomers with tailored yield strength and toughness.[3] However, these compositions and their variants, primarily based on plastic and rubbers with nitrile functionality, exhibit neither an acceptable melt flow index nor ductility. Because of the high molecular weight rubbery components, the composition shows very high viscosity; rapid processing of these materials remains a challenge. By contrast, glassy nitrile plastics become more brittle once lignin is incorporated. To address these challenges, ORNL and Prisma Renewable Composites, Inc. (Prisma), devised the incorporation of compatibilizers or processing aids in the composition.

Prisma is developing and commercializing replacement materials to today's purely petrochemical plastics. These alternative materials consist of renewable polymers based on lignin. The first such material Prisma is bringing to market is an ABS resin system that includes lignin. After establishing encouraging progress toward its goals, Prisma identified a large-scale commercial partner that was interested in the ABS-lignin material. The commercial partner provided detailed material property requirements that would indicate acceptability, allowing Prisma to focus its R&D efforts. ORNL was tasked with providing some of the analysis of various properties as Prisma worked to formulate improvements. Initial studies of these composite blends indicated acceptable processing, but some mechanical properties may need further improvement.

This program aimed to develop compositions based on different lignin fractions loaded in nitrile-containing polymers to meet the expectations and commercial interest of Prisma via two pathways that address the identified needs. The first, which was the path developed by Prisma, is to modify an existing

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[1] Akato, K., Tran, C. D., Chen, J., Naskar, A. K. "Poly(ethylene oxide)-Assisted Macromolecular Self-assembly of Lignin in ABS Matrix for Sustainable Composite Applications." *ACS Sustainable Chemistry & Engineering* 3(12) 3070–3076 (2015).

[2] Naskar, A. K, Tran, C. D. High Performance Lignin-Acrylonitrile Polymer Blend Materials (ORNL ID 3426) U.S. Patent Appln. No. 14/798,729 (2015).

[3] Tran, C. D., Chen, J., Keum, J. K., Naskar, A. K. "A New Class of Renewable Thermoplastics with Extraordinary Performance from Nanostructured Lignin-Elastomers." *Advanced Functional Materials* 26(16) 2677–2685 (2016).

polymer of interest (ABS) that has good melt flow properties by blending lignin to achieve a desirable renewable content and range of mechanical properties. The second pathway is to formulate and produce blends of lignin with nitrile rubbers to create new materials that have a commercially attractive balance of processability and mechanical properties. The COVID-19 pandemic significantly affected this research, necessitating that the team focus on the first pathway only.

2. OBJECTIVES

The overarching goal of this Cooperative Research and Development Agreement was to control the morphology and interfacial structure between lignin and polymer matrix systems to facilitate successful industrial adoption and commercialization. This work aimed to improve processing characteristics of lignin-based compositions. Appropriate test protocols have been established.

The following tasks were undertaken in this research.

Task 1: Optimize composite blends of lignin with commercial ABS

This task defined blends that contain at least 25% lignin in a commercial ABS and retain sufficient ductility for use in Prisma's customer applications by incorporating plasticizers and/or compatibilizers and process optimization.

Task 1.1: Formulate test compositions by melt-mixing method

This work used Prisma-supplied lignins, compatibilizers, and ABS resin. Using compositions and processability criteria developed by ORNL and Prisma, Prisma prepared test blends on a Brabender extruder.

Task 1.2: Evaluation of product performance

This task was jointly led by ORNL and Prisma. The compositions prepared in Task 1.1 were mechanically tested and rheologically characterized. Prisma analyzed the results of the selected compositions.

Task 1.3: Scaled-up production of compounded resin

This task was jointly led by ORNL and Prisma. The goal was to produce one or two selected resin compositions based on lignin blends that offered superior mechanical performance and acceptable processability.

3. RESULTS AND DISCUSSION

3.1 COMPOSITIONS INVESTIGATED

Prisma supplied the lignin powder, which was used as-received for compounding with polymers. A representative scanning electron micrograph of the lignin powder is displayed in Figure 1. The compositions investigated by the team are listed in Table 1. For compatibilization between ABS and lignin, different viscosity modifiers and compatibilizers were mixed at 3, 5, and 10 parts of additive per 100 resin loadings.

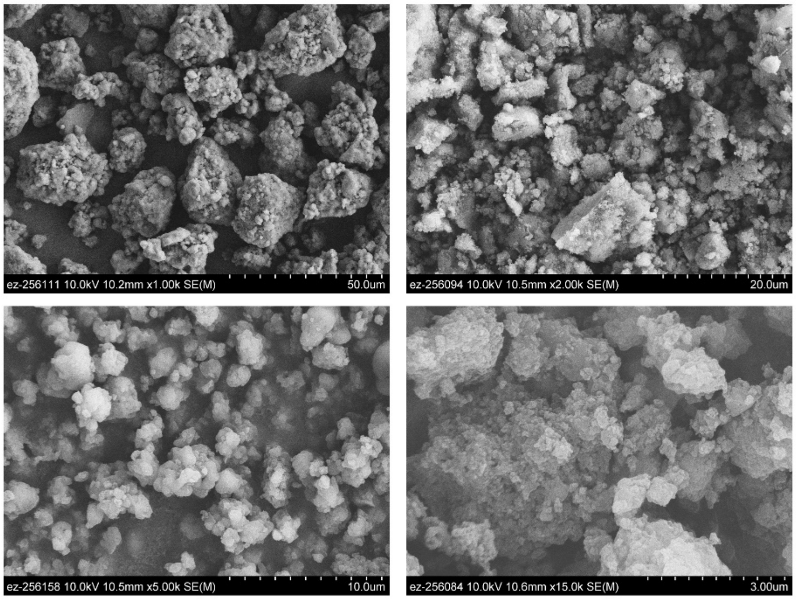

Figure 1. Scanning electron micrographs of lignin powder showing self-assembly of hydrogen-bonded amorphous lignin particles.

Table 1. Various lignin–ABS mixtures prepared with and without additives

	Formulation (parts per 100 resin)			
Sample ID	**Lignin**	**ABS**	**Additive**	
DW02-58-1	25	75	0	Additive #1
DW02-58-2	25	75	3	Additive #2
DW02-59-1	25	75	3	Additive #3
DW02-59-2	25	75	3	Additive #4
DW02-60-1	25	75	3	Additive #5
DW02-60-2	25	75	5	Additive #5
DW02-60-3	25	75	5	Additive #2
DW02-60-4	25	75	5	Additive #3
DW02-60-5	25	75	5	Additive #6
DW02-61-1	25	75	5	Additive #1
DW02-61-2	25	75	5	Additive #4
DW02-62-1	25	75	3	Additive #7
DW02-62-2	25	75	5	Additive #7
DW02-62-3	25	75	10	Additive #7
DW02-63-1	25	75	10	Additive #3
DW02-63-2	25	75	10	Additive #6
DW02-63-3	25	75	10	Additive #1
DW02-63-4	25	75	10	Additive #5
DW02-63-5	25	75	10	Additive#2
DW02-65-2	25	75	10	Additive #8
DW02-65-3	25	75	10	Additive #9
DW02-65-4	25	75	10	Additive #10
DW02-66-1	25	75	10	Additive #4

Based on the findings from these compositions, new samples were prepared and tested. Details of those proprietary compositions are shown in this report. The overall performance was good, so selected samples were scaled up for injection molding and subsequent impact testing.

3.2 RHEOLOGICAL PROPERTIES

The additives used in this study were viscosity modifiers. The goal was to improve processability of lignin-loaded composites for rapid manufacturing to improve and ductility of the manufactured parts. Figure 2 shows evidence of degassing (and bubble formation) from a compounded mixture when the sample is placed in a preheated rheometer.

Figure 2. Bubbles formed on the surface during initial heating in the rheometer (before sample was cleaned to match plate diameter).

Figure 3 displays storage modulus vs. angular frequency plots for 75/25 ABS/lignin compositions containing 10 parts of additive per 100 parts of resin of different additives. The different additives play different roles in melting behavior. For impact strength enhancement, a networked structure along with matrix softening was desired. Figure 3 shows that most of the additives effectively form networked morphologies that enhance the corresponding storage modulus and slope at the terminal (low-frequency region), except additive #4 that mostly acts as diluent plasticizer.

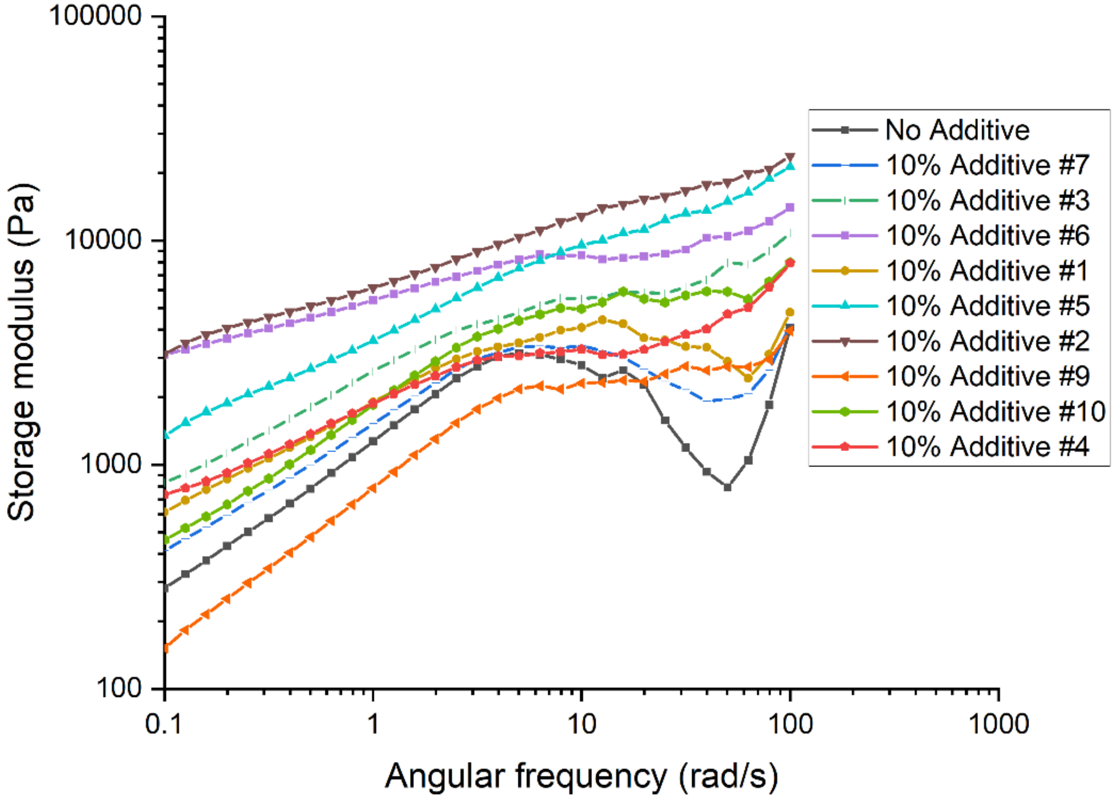

Figure 3. Storage modulus vs. angular frequency plots for 75/25 ABS/lignin compositions containing 10 parts of additive per 100 parts of resin. The samples were dynamically sheared at 210°C at 2% strain from 0.1 to 100 Hz frequencies between 8 mm parallel plates and 0.5 mm gap in a Discovery Hybrid Rheometer-3 (TA Instruments).

Representative dynamic mechanical loss tangent data for the samples in Table 1 are displayed in Figure 4. The samples were scanned from −100°C to 150°C at 0.005% strain and 1 Hz frequency using a rectangular bar under three-point bending mode. The peak in loss tangent spectra indicates glass transition temperature of the compositions. All compositions show softening or reduced glass transition temperature.

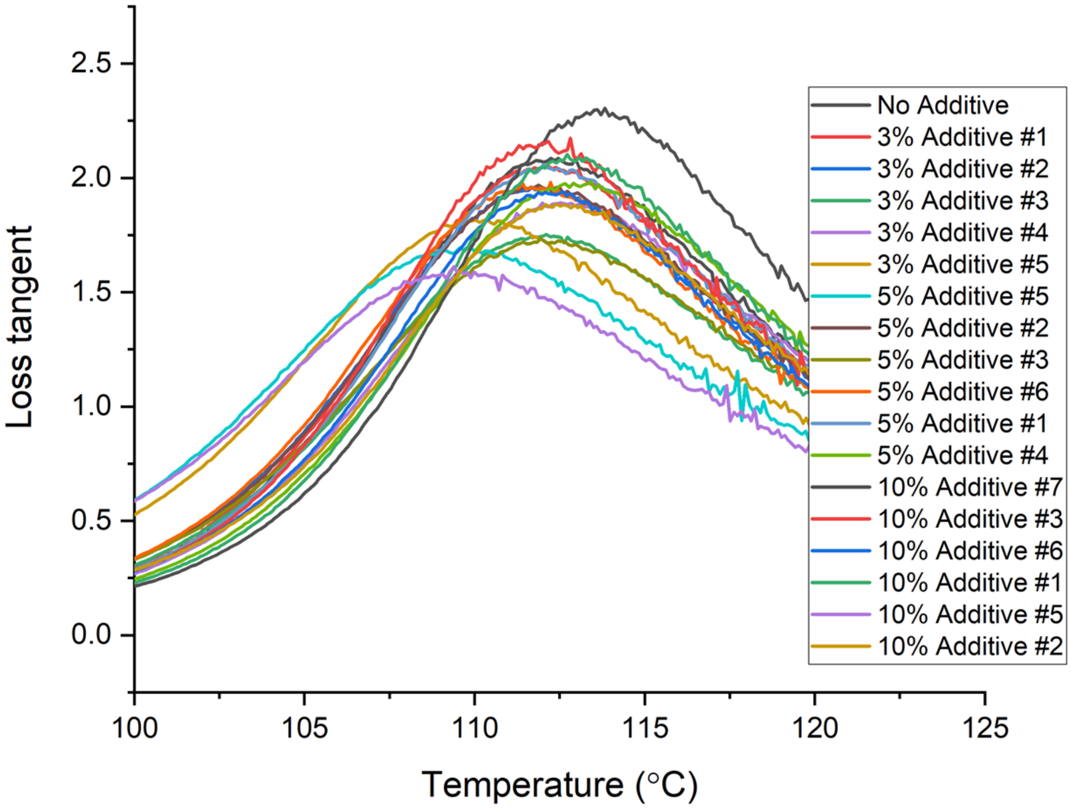

Figure 4. Dynamic mechanical loss tangent spectra of the samples showing peak temperature as the glass transition temperature. The samples were scanned from −100°C to 150°C at 0.005% strain 2°C ramp rate and 1 Hz frequency using a rectangular bar under three-point bending mode in a Discovery Q800 DMA device (TA Instruments).

3.3 MORPHOLOGY BY SCANNING ELECTRON MICROSCOPY

Selected samples were scaled up for injection molding and subsequent impact testing. Representative scanning electron micrographs of injection-molded specimens are displayed in Figure 5. The goal was to discover whether lignin forms large, discrete domains during high-shear processing of the compositions. However, specific injection-molded samples had large lignin domains (some over 2 µm) present throughout the matrix. Therefore, new compositions involving small molecular weight lignin–ABS compatibilizing agents were investigated. Specifically, maleic anhydride was used with and without rubber- and organic peroxide–based crosslinkers (e.g., dicumyl peroxide). Based on multiple scaled-up compounding and injection molding trials, specific compositions containing Additive #3 delivered smaller lignin domains, as shown in Figure 6.

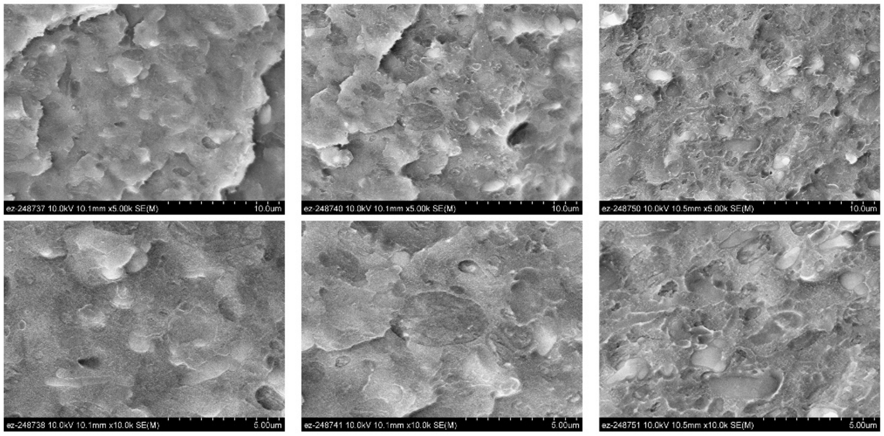

Figure 5. Scanning electron micrograph of injection-molded samples of ABS with 5% Additive #11, 5% Additive #12 showing larger lignin domains within the ABS matrix.

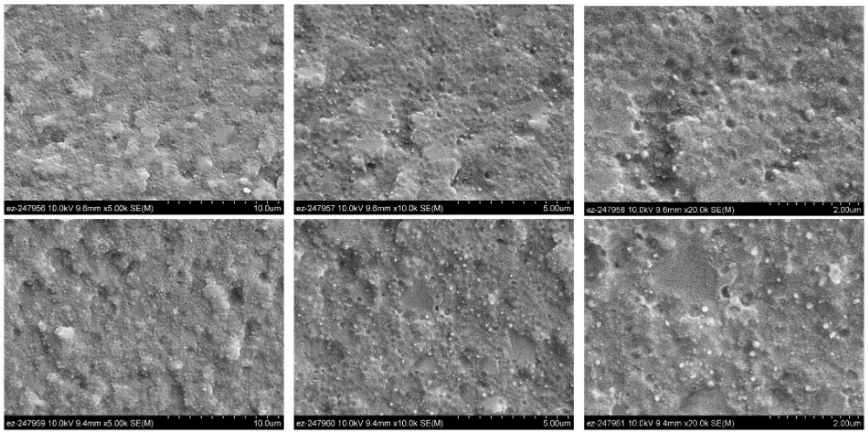

Figure 6. Scanning electron micrograph of injection-molded samples of ABS with 10% Additive #3 showing smaller lignin domains within the ABS matrix.

4. CONCLUSIONS

These results enabled Prisma to design a cost-effective compatibilized composition that contained more than 20 wt % lignin in an ABS matrix. This composition delivered at least 50% greater notched izod impact strength and/or 50% greater elongation at break compared with the baseline composition without any compatibilizer. The technology finally led to development of an injection moldable automotive composite that contains 20% or higher renewables and meets performance requirements.