DEVELOPMENT OF HIGH-PERFORMANCE BIOMASS COMPOSITES USING A PA11/GLYCOL LIGNIN MATRIX

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ABSTRACT

Polyamides (PA, “nylon”) is a class of thermoplastic polymers characterized by good heat/chemical resistance, mechanical properties, and processability, leading to widespread use in various automotive components. The two most common varieties, PA6 and PA66, are petroleum-based and carry a relatively large carbon footprint. Thus, bio-based alternatives such as PA11 have been introduced in recent decades. However, these polymers tend to have longer alkyl chains and exhibit lower mechanical properties than their traditional counterparts. In this work, glycol-modified lignin (GL) biomass is added to PA11 to create a blended matrix for short-carbon fiber composites in order to improve performance while maintaining a high biomass content. Characterization of the structure and properties of the resulting blends shows that PA11 and GL are highly compatible with uniform dispersion, which is essential for improving mechanical properties without sacrificing processability. Furthermore, the tensile modulus and strength of the short-fiber composites containing lignin exceeds that expected from the rule of mixtures, reaching performance comparable to super engineering plastic compounds like PEEK/GF30. The applicability of these biomass composites for more sustainable automotive components is discussed.

1 INTRODUCTION

The growing demand for sustainable materials has accelerated the development of biomass-based composites, particularly those using bio-derived plastics and additives. These composites offer a compelling alternative to conventional petroleum-based materials, driven by the need for environmentally friendly options that also deliver high performance in demanding applications. Recent advances have focused on incorporating bio-derived thermoplastics, such as polylactic acid (PLA), polyhydroxyalkanoates (PHA), and bio-based polyamides (PA11, PA1010, etc), into composite formulations [1-7]. These bio-based matrices not only address environmental concerns but also provide high mechanical properties, making them viable candidates for industries ranging from automotive to electronics and aerospace.

However, despite these advancements, there remain several challenges in bringing them into high-performance applications. Bio-derived plastics often exhibit limitations in processing, thermal stability, and mechanical properties compared to their petroleum-based counterparts. Issues like brittleness, low-temperature performance, and moisture sensitivity can hinder their widespread adoption, especially in demanding environments where durability and reliability are essential [5,6]. Furthermore, achieving uniformity and consistency in the bio-plastic matrix during composite fabrication, while maintaining environmental sustainability, presents significant technical challenges. In the specific case of PA11, its long alkyl segment and relatively low hydrogen bond (HB) density compared to conventional PA6 gives it low modulus (~1.5 GPa) and strength (~40 MPa). Thus, simply adding reinforcing fibers will not make

it competitive with conventional engineering plastic composites. Overcoming these barriers requires innovative approaches to both material design and manufacturing techniques.

In this context, lignin, a natural polymer obtained as a byproduct of the pulp and paper industry, has gained attention as a promising additive in biomass-based composites [8]. Lignin's complex aromatic structure and high antioxidant properties make it a suitable candidate for enhancing the performance of petroleum- and bio-derived polymers alike [9]. Recent studies have shown that lignin can significantly improve the oxidative stability of polyolefins [10] and PA6 [11], protecting the material from degradation under UV exposure and high temperatures. Additionally, lignin can enhance the mechanical properties of composites by acting as a reinforcing agent [10]. However, the main issue impeding widespread use is the typically poor compatibility with many polymers used in composites. The phenolic and hydroxyl groups in lignin have the potential to interact with functional groups on the host polymer and thus increase tensile strength and modulus. Various approaches to improve lignin's dispersibility such as alkyl, acetyl, and hydroxyl modifications have been met with varying degrees of success [12,13].

This work reports the fabrication of PA11/carbon fiber (CF) composites using a PEG-grafted glycol lignin (GL) in a scalable melt-mixing process. Synergistic interactions between the three constitutents lead to unprecedented improvements in tensile modulus and strength, rivalling conventional super engineering plastics like PPS and PEEK. Material characterization results and implications for future work are discussed.

2 EXPERIMENTS

2.1 Materials and fabrication

The polymer used in this study was an unreinforced, standard-grade PA11 (BML OTLD, Arkema). The glycol lignin (GL) was produced by acid-catalyzed PEG solvolysis of softwood biomass yield lignin derivatives grafted with about 26 wt% PEG400, as described elsewhere [14]. Chopped carbon fibers (PYROFIL™ TR06NLB5K) having length of roughly 6 mm and diameter of about 7 μm were purchased from Mitsubishi Chemical.

PA11 and GL were both dried at 90 °C for 24 hr before blending in a twin-screw extruder (S1KRC, Kurimoto) at 240-250 °C. Blends containing different amounts of GL and CF ranging from 0-30 wt% were then injection molded (Mini JET II, Thermo Scientific) into ISO 527-2 dumbbell specimens at cylinder and mold temperatures of 230 °C and 80 °C, respectively. No other heat treatments were applied before characterization.

2.2 Characterization

Mechanical behavior was evaluated by tensile testing according to ASTM D638 using an electromechanical testing machine (EZ-LX, Shimadzu) equipped with a 5kN load cell and video extensometer, at a crosshead speed of 5 mm/min. FTIR spectra were collected at room temperature over the range 500-4000 cm^{-1} in ATR mode (IR Affinity, Shimadzu).

Differential scanning calorimetry (DSC7020, Hitachi Hi Tech) was performed over the range 20-250 °C at a heating/cooling rate of 10 °C/min, using 2-3 mg of sample. The crystallinity (X_c) was approximated by the equation:

$$X_c = \frac{\Delta H_m}{(1-f)\Delta H_m^0} \quad (1)$$

where f is the mass fraction of filler (e.g., GL), and ΔH_m and ΔH_m^0 are the melting enthalpies of the specimen (taken from the first DSC scan) and a perfect crystal (taken as 220 J/g [15]), respectively.

3 RESULTS

3.1 Composite fabrication and structure

Melt-mixing of the blends and composites was successfully performed in a twin-screw extruder, without significant changes in processibility even up to 20 wt% GL loading, although an increase was noticed for 30 wt% GL loading. Figure 1 depicts the fabrication process along with a schematic of the expected material structure. The abundant hydroxyl groups on lignin, supplemented with grafted PEG chains allows for polar and HB interactions between GL and PA11. Additionally, the aromatic backbone of lignin should exhibit high affinity for the surface of carbon fibers.

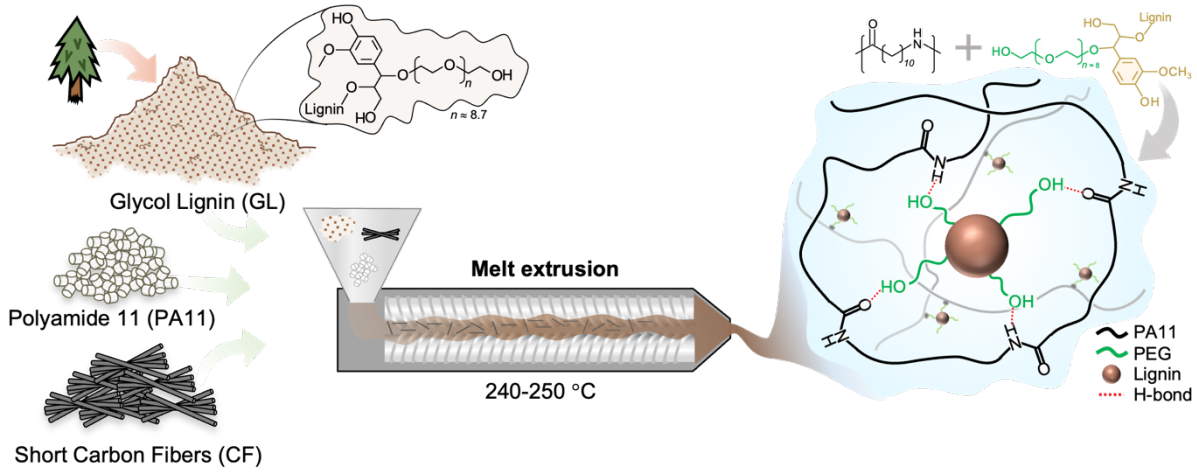

Figure 1: Fabrication of short-carbon fiber composites using PA11/GL blends via melt-mixing, with the proposed polymer/lignin interactions.

FTIR did not show significant presence of GL, despite the substantial loading (0-30 wt), but slight shifts in the carbonyl region of amide II (1640 cm^{-1}) indicated HB interaction. FTIR can be useful for studying HB interactions in polymers, but the changes tend to be small when comparing different forms of H-bonds, rather than the increase or decrease in their number. Recent work has indicated that GL may form H-bonds with polyamide in a disordered configuration, which does not appear the same as so-called "free" carbonyls [11]. The melting temperatures and enthalpies shifted noticeably with increasing GL content (Figure 2), which can be attributed to a change in the crystal phase composition due to the presence of lignin [11]. In addition, the crystallinity increased by several percent while the crystallization temperature decreased by several degrees, which indicates that lignin has a retardation effect that promotes slower crystal growth (Table 1).

Sample	T_m (°C)	T_c (°C)	X_c (%)
PA11	189.7	159.5	28.3
PA11-GL10	187.9	157.8	28.5
PA11-GL20	187.7	154.5	29.5
PA11-GL30	187.4	153.7	30.1

Table 1: Thermal properties of PA11/GL blends.

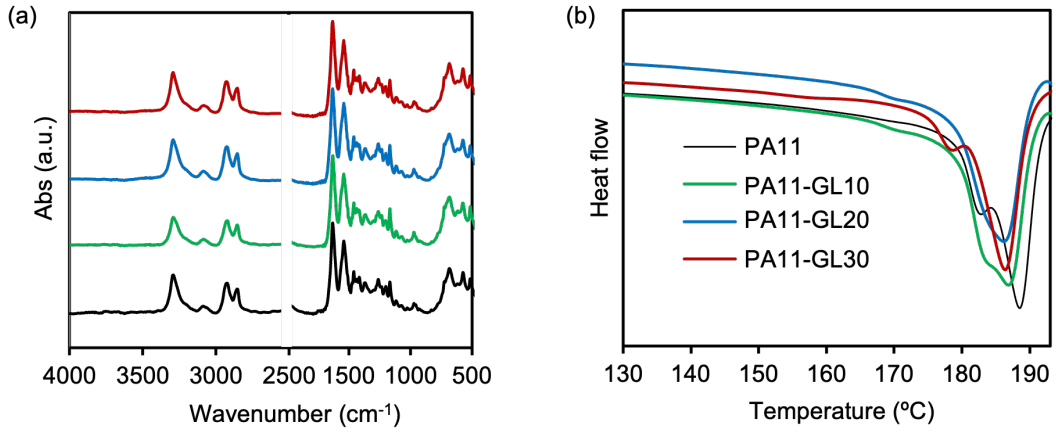

Figure 2: (a) FTIR spectra and (b) DSC thermograms of PA11/GL blends.

3.2 Tensile properties

The addition of GL alone did not significantly increase the tensile strength or modulus of PA11 until 30 wt% loading, as seen in Figure 3(a,b). The failure strain was for 10 wt% GL blends did not change drastically, and although higher GL content resulted in lower failure strains compared to neat PA11, over 100% was still achieved at 30 wt% GL.

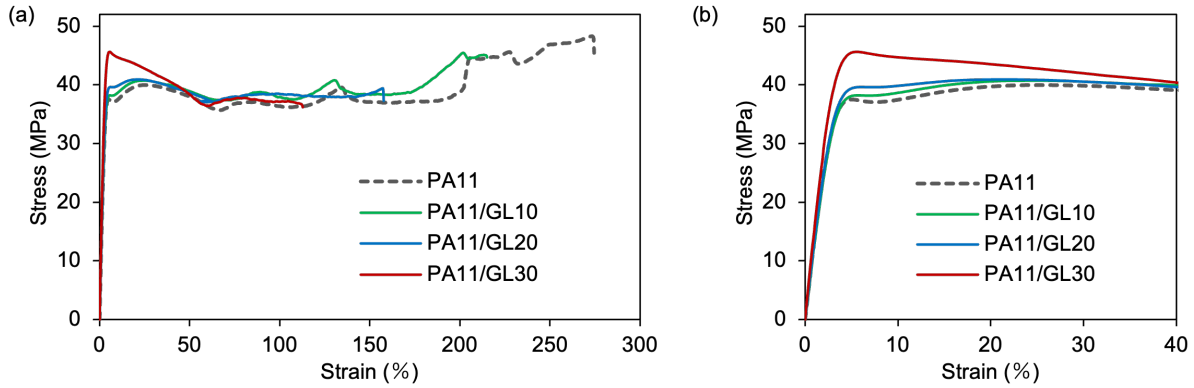

Figure 3: Stress-strain curves for PA11/GL blends for the (a) full and (b) elastic strain regions. (c) Stress-strain curves for PA11/CF composites. Stress-strain curves of biomass composites fixed at (d) 10 wt% CF and (e) 20 wt% CF to highlight the effect of lignin.

Figure 4(a) shows typical tensile behavior of short-fiber composites was observed for PA11/CF. Despite the minimal reinforcing effect of GL on PA11, a drastic improvement in reinforcing efficiency was observed for the biomass-matrix short fiber composites. This is demonstrated in Figure 4(b) by fixing CF at 10 wt% whereby the strength increases by 10% and 40% for GL loadings of 10 wt% and 20 wt%, respectively. The same trend is observed for 20 wt% CF composites in Figure 4(c). Such a drastic synergistic reinforcing effect has never been reported in the literature before, although a similar (but less drastic) effect was reported for PP/GL composites [9]. This suggests that PEG-grafted glycol lignin possesses a unique ability to aid in stress transfer between fibers. The full set of data for all composites in the study is summarized in Figure 4(d,e), with comparison to typical values of PEEK-GL30 for reference. In particular, an exceptionally high modulus of 16 GPa was achieved for the GL30-CF30 composite (70% biomass by weight), which is (to the authors' knowledge) the highest reported for a high-biomass-content composite.

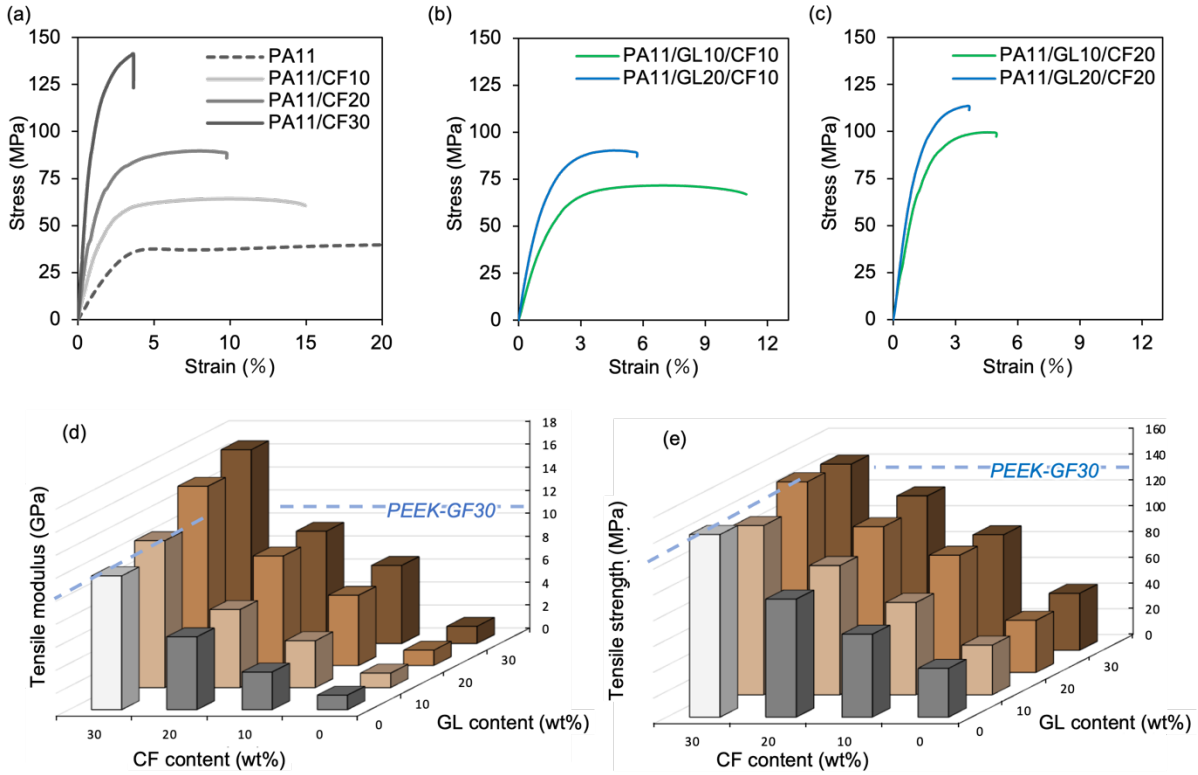

Figure 4: (a) Stress-strain curves for PA11/CF composites. Stress-strain curves of biomass composites fixed at (b) 10 wt% CF and (c) 20 wt% CF to highlight the effect of lignin. Summarized results for (d) tensile modulus and (e) tensile strength for all composites in this study.

9 CONCLUSIONS

In this study, all-biomass matrix materials of PA11 and PEG-grafted glycol lignin were prepared by scalable melt-mixing, then combined with short carbon fibers to create biomass composites. Polar and HB interactions between the GL and PA11 did not significantly increase the tensile properties of the polyamide itself, but the blend exhibited a synergistic reinforcing effect that drastically improved the tensile properties of the short fiber composites. The tensile modulus for some blends reached levels similar to PEEK-GF30. More study is needed to understand the detailed mechanisms of how lignin influences crystallization and deformation behavior of PAs, but this work demonstrates that PA11/GL composites have potential for high-performance applications.

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REFERENCES

[1] A.K. Mohanty, S. Vivekanandhan, J.-M. Pin and M. Misra, Composites from renewable and sustainable resources: challenges and innovations, *Science*, **362**, 2018, pp. 536-542, (doi: 10.1126/science.aat9072).

[2] R. Chen, M.A. Abdelwahab, M. Misra and A.K. Mohanty, Biobased ternary blends of lignin, poly(lactic acid), and poly(butylene adipate-co-terephthalate): The effect of lignin heterogeneity on blend morphology and compatibility, *Journal of Polymers and the Environment*, **22** , 2014, pp. 439-448, (doi: 10.1007/s10924-014-0704-5).

[3] M. Li, Y. Jia, X. Shen, T. Shen, Z. Tan, W. Zhuang, G. Zhao, C. Zhu and H. Ying, Investigation into lignin modified PBAT/thermoplastic starch composites: thermal, mechanical, rheological and water absorption properties, *Industrial Crops and Production*, **171**, 2021, pp. 113916, (doi: 10.1016/j.indcrop.2021.113916).

[4] M.A.S. Anwer, H.E. Naguib, A. Celzard and V. Fierro, Comparison of the thermal, dynamic mechanical and morphological properties of PLA-lignin & PLA-tannin particulate green composites, *Composites Part B*, **82**, 2015, pp. 92-99. (doi: 10.1016/j.compositesb.2015.08.028).

[5] Y.-L. Chung, J.V. Olsson, R.J. Li, C.W. Frank, R.N. Waymouth, S.L. Billington and E.S. Sattely, A renewable lignin-lactide copolymer and application in biobased composites, *ACS Sustainable Chemistry and Engineering*, **1**, 2013, pp. 1231-1238, (doi: 10.1021/sc4000835).

[6] S.-J. Xiong, B. Pang, S.-J. Zhou, M.-K. Li, S. Yang, Y.-Y. Wang, Q. Shi, S.-F. Wang, T.-Q. Yuan, R.-C Sun, Economically competitive biodegradable PBAT/lignin composites: effect of lignin methylation and compatibilizer. *ACS Sustainable Chemistry and Engineering*, **8**, 2020, pp. 5338-5346, (doi: 10.1021/acssuschemeng.0c00789).

[7] M.A. Abdelwahab, S. Taylor, M. Misra and A.K. Mohanty, Thermo-mechanical characterization of bioblends from polylactide and poly(butylene adipate-co-terephthalate) and lignin, *Macromolecular Materials and Engineering*, **300**, 2015, pp. 299-311, (doi: 10.1002/mame.201400241).

[8] Future Markets, Inc., The Global Market for Lignin 2021-2031 (Report 5331648). https://www.futuremarketsinc.com/the-global-market-for-lignin-2021-2031/, 2022 (accessed 5 May 2022).

[9] J. Tanks, K. Tamura, K. Naito, T.T. Nge and T. Yamada, Glycol lignin/MAH-g-PP blends and composits with exceptional mechanical properties for automotive applications, *Composites Science and Technology,* **238**, 2023, pp. 110030 (doi: 10.1016/j.compscitech.2023.110030).

[10] J. Tanks, K. Tamura, K. Naito, T.T. Nge and T. Yamada, Durable and recyclable biomimetic glycol lignin/polyolefin compounds for a circular economy, *Journal of Materials Chemistry A,* **12**, 2023, pp. 3014-3025 (doi: 10.1039/D3TA06230A).

[11] J. Tanks, T. Akagawa, K. Tamura, Y. Nemoto, K. Naito, T.T. Nge, Y. Watanabe and T. Yamada, Enhancing the thermo-oxidative stability of polyamide 6 by scalable melt-blending with PEG-grafted glycol lignin, *Polymer,* **accepted**, 2025.

[12] P. Buono, A. Duval, P. Verge, L. Averous and Y. Habibi, New insights on the chemical modification of lignin: Acetylation versus silylation, *ACS Sustainable Chemistry and Engineering*, **4**, 2016, pp. 5212-5222, (doi: 10.1021/acssuschemeng.6b00903).

[13] H. Sakai, K. Kuroda, S. Muroyama, T. Tsukegi, R. Kakuchi, J. Takada, A. Hata, R. Kojima, T. Ogoshi, M. Omichi, K. Ninomiya, K. Takahashi, Alkylated alkali lignin for compatibilizing agents of carbon fiber-reinforced plastics with polypropylene, *Polymer Journal*, **50**, 2018, pp. 281-284, (doi: 10.1038/s41428-017-0009-3).

[14] T.T. Nge, Y. Tobimatsu, S. Takahashi, E. Takata, M. Yamamura, Y. Miyagawa, T. Ikeda, T. Umezawa and T. Yamada, Isolation and characterization of polyethylene glycol (PEG)-modified glycol lignin via PEG solvolysis of softwood biomass in a large-scale batch reactor, *ACS Sustainable Chemistry and Engineering*, **6**, 2018, pp. 7841-7848, (doi: 10.1021/acssuschemeng.8b00965).

[15] K. Jariyavidyanont, A. Janke and R. Androsch, Crystal self-nucleation in polyamide 11 of different semicrystalline morphology, *Polymer*, **184**, 2019, pp. 121864 (doi: 10.1016/j.polymer.2019.121864).