



Phototunable Lignin Plastics to Enable Recyclability

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The accumulation of non-degradable petrochemical plastics imposes a significant threat to the environment and ecosystems. We addressed this challenge by designing a new type of phototunable plastics based on the unique lignin chemistry to enable readily end-life recycling. The advanced material design leveraged the efficient photocatalytic lignin depolymerization by ZnO nanoparticles to build lignin-polymethyl methacrylate (PMMA)-ZnO blends. We first demonstrated the highly effective phototunable lignin depolymerization in the complex polymer blend matrix and explored the molecular mechanisms. The technical barriers of mechanical property and recycling processing were then addressed by a new blend design with lignin core grafted with PMMA polymer. The new process has resulted

in a new type of PMMA-*g*-lignin blend, which significantly improved the mechanical properties, making it comparable to PMMA alone. More importantly, the mechanical properties of the UV-treated blend decreased drastically in the new design, whereas the properties did not reduce in the non-grafted blends upon UV exposure. The results highlighted that the new blend design based on graftization maximized the impact of lignin depolymerization on blend structure and recyclability. Based on the results, we developed a process integrating UV and alkaline treatments to recycle PMMA for plastics and fractionated lignin for bioconversion or other applications in the new phototunable plastics.

Introduction

The accumulation of petrochemical plastics that are highly recalcitrant to degradation represents one of the most predominant challenges in sustainability.^[1] This environmental crisis results from the chemical design of current industrial polymers without consideration of their end of life consequences.^[1,2] In particular, plastics containing highly inert chemical bonds such as C–C and C–H bonds are utilized, with abundant yet unsustainable feedstock from petrochemical industries.^[2a] Different approaches have been sought after plastics manufacturing to address significant environmental challenges associated with

petroleum-based plastics including a) reduction of environmental contamination through enhanced recyclability at the end of service life, b) the utilization of low-cost, yet renewable feedstock for plastics production, and c) producing biodegradable bioplastic.^[3] Biopolymers like lignin and cellulose have unique potential for manufacturing both recyclable and renewable plastics to address these environmental challenges. Unlike petroleum-based monomers, biopolymers like lignin have abundant ethyl ether bonds that can easily depolymerized toward recycling and/or upcycling.^[2a]

Lignin, the second most abundant biopolymer on earth, can be utilized as a feedstock to blend with polymers such as

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polyethylene (PE), polypropylene (PP), polyethylene terephthalate (PET), polyethylene-vinyl acetate (EVA), polymethylmethacrylate (PMMA), and polylactic acid (PLA) to produce bioplastics with improved renewability and degradability.^[4] The unique photodegradation characteristic of lignin could facilitate the recyclability of conventional plastics. Even though lignin has a UV absorption peak and could degrade to small molecules under certain photoirradiation conditions, the reaction rate is too slow and the efficiency is too low to be applied towards biodegradation. Various catalysts have been demonstrated to show improvement such degradation efficiency. Cadmium sulfide/titanium dioxide (CdS/TiO₂) nanoparticles can serve as catalysts in an aqueous solution and vastly accelerate the degradation,^[5] and the TiO₂ photocatalytic system can be active under solventless conditions.^[6] The ·OH radicals produced during the photocatalytic reaction are considered the main reactive species.^[5b,7] ZnO is a suitable alternative to TiO₂ since it has a similar photodegradation mechanism to that of TiO₂ but is more cost-effective and with less environmental concern. Thus, we have designed phototunable plastics with lignin as a major component and ZnO as the catalysts.

Among the different guest polymers to be used blended with lignin, we decided to first study the lignin-PMMA-ZnO blend to evaluate the concept of phototunable plastics for recyclability. Poly(methyl methacrylate), also known as acrylic, is widely used to replace glass due to its high transparency and good mechanical properties. PMMA offers a good balance of tensile strength, flexural strength, transparency, polishability, and UV tolerance. Hydrogen bonding formed between the lignin and carbonyl groups of PMMA is expected to result reasonable compatibility and dispersion of lignin in the PMMA matrix, which is needed for retaining the PMMA properties.

In direct blends, lignin was dispersed in the polymer matrix as droplets and complete miscibility is prevented by the self-interactions of lignin molecules.^[8] Adding small molecule plasticizers can space the lignin chains apart and thus weaken the self-interactions of lignin.^[9] And grafting of lignin as a copolymer can greatly improve the miscibility of lignin into a polymer matrix.^[10] Atom transfer radical polymerization (ATRP) and reversible addition-fragmentation chain transfer (RAFT) are the most widely used in lignin graft polymerization. The esterification of lignin hydroxyl groups is generally used as the macroinitiators for polymerization. The lignin copolymers normally have improved mechanical performance.^[11]

In this study, we will first evaluate the concept of phototunable plastics containing lignin, PMMA, and ZnO nanoparticles. We will then further investigate lignin's degradability and associated mechanisms. The mechanical properties of the PMMA/lignin blend was further evaluated and improved with various strategies.

Results and Discussion

Miscibility and compatibility of lignin-PMMA-ZnO polymer blend

In order to determine if ZnO can serve as an efficient catalyst in lignin-based plastics blend, we have first developed lignin-PMMA blends containing ZnO and evaluated the photodegradation of the lignin components in the new blend. Lignin selection was based on previous studies of lignin chemistry. Various fractionation technologies were developed to render the lignin with more processibility for bioconversion,^[12] carbon materials,^[13] nanomaterials^[14] and others.^[15] We selected the lignin derived from combinatory pretreatment of lignocellulosic biomass, because the lignin is water soluble, has a relatively low molecular weight, and is biorefinery compatible. In particular, the small molecular weight and solubility allow the hydrogen bonds to form between the lignin and PMMA (Figure 1A1). The utilization of biorefinery lignin also makes it possible to develop recyclable plastics as a value-added product for lignocellulosic biorefinery.^[16]

Sheets made of lignin-PMMA blend and lignin-PMMA-ZnO blend were prepared by blending 10% lignin by weight or 10% lignin and 0.5% ZnO nanoparticles (5 nm in diameter)^[17] with a commercial PMMA, respectively. Optical microscopy images were acquired on the PMMA-ZnO blend, lignin-PMMA blend, and lignin-PMMA-ZnO blend sheets to determine the compatibility of lignin and ZnO nanoparticles with PMMA. As shown in Figure 1A2, the PMMA-ZnO sheet was highly transparent, and no detectable ZnO nanoparticle aggregates can be seen. The lignin-PMMA blend sheet had a dark brown color, and dark dots could be seen under Optical microscopy (Figure 1A3), which suggested good dispersion of lignin domains in PMMA. The lignin-PMMA-ZnO blend showed a similar pattern to the lignin-PMMA sheet (Figure 1A4). Lignin-PMMA-ZnO had a thickness of 0.101 mm, whilst the thickness of lignin-PMMA was 0.890 mm. Under scanning electron microscopy (SEM), the lignin-PMMA-ZnO blend had no visible defects on the surface (Figure 1B), indicating great miscibility among the PMMA, lignin, and ZnO nanoparticles. Elemental mapping was carried out to examine the presence of ZnO incorporation in the polymer blends. As shown in Figure 1C, the Zn elements were found to distribute uniformly in the lignin-PMMA-ZnO film as the C and O elements did, which indicates that ZnO nanoparticles were well distributed in the lignin-PMMA-ZnO polymer blends. All the above data demonstrated that lignin-PMMA-ZnO blend had good compatibility and uniformity.

Efficient degradation of lignin in the lignin-PMMA blend enabled by photocatalytic ZnO

We further analyzed the phototunable lignin depolymerization in various blends to prove the concept of phototunable bioplastics. Both UV/Vis absorbance and the heteronuclear single quantum coherence – nuclear magnetic resonance (HSQC-NMR) were carried out to evaluate the lignin depolymer-

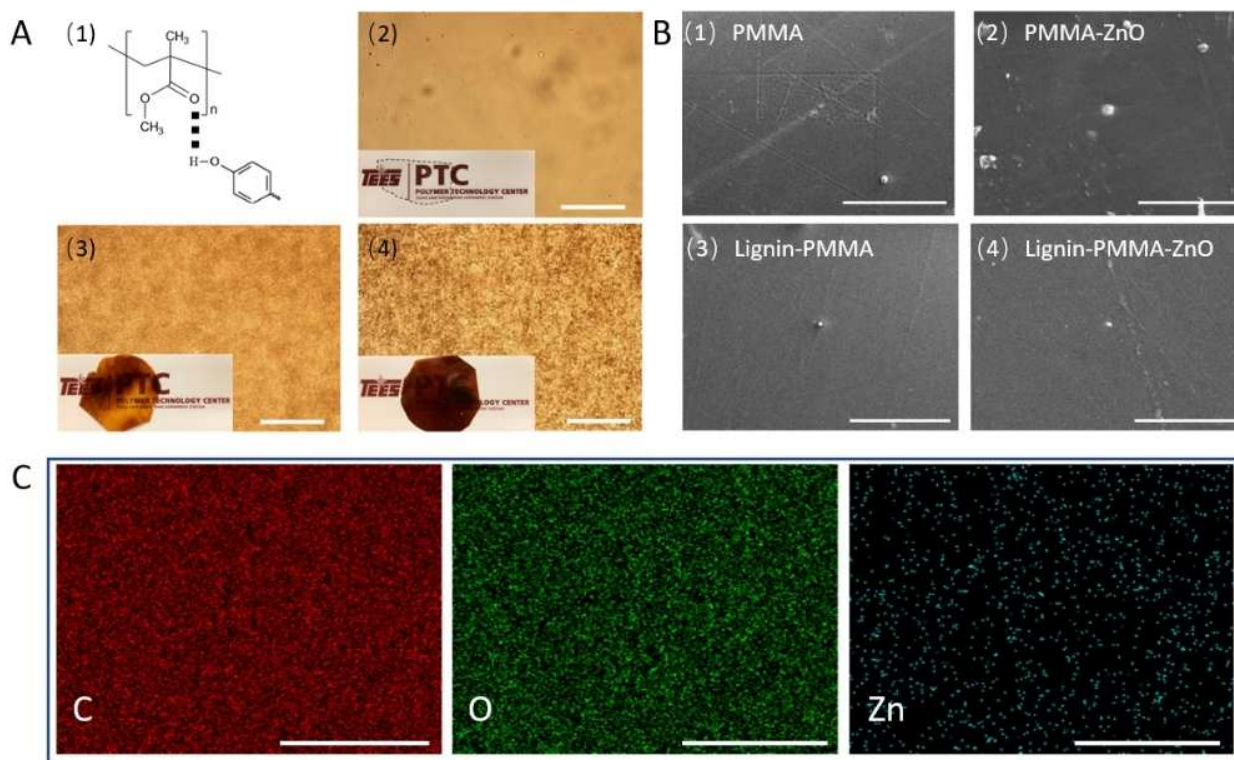


Figure 1. Preparation and characterization of lignin-PMMA-ZnO blend. (A1) schematic diagram of H-bond forming between PMMA and lignin molecule; optical microscopy images and photos of lignin-PMMA blend samples: (A2) PMMA-ZnO blend, the edge in the left bottom photo was marked using a dotted line; (A3) lignin-PMMA blend; (A4) lignin-PMMA-ZnO blend. SEM images of various polymer blends: (B1) Commercial PMMA, (B2) PMMA-ZnO blend, (B3) lignin-PMMA blend, (B4) lignin-PMMA-ZnO blend. (C) Element mapping for lignin-PMMA-ZnO nanoparticle blends. All scale bars correspond to 50 μm in this figure.

rization within the polymer blends. Upon the UV exposure, PMMA sheet showed a strong absorbance peak at 232 nm and transmittance at around 260 nm (Figure S1 in the Supporting Information). Lignin-PMMA and lignin-PMMA-ZnO blends had a wider absorbance between 200 nm and 400 nm, and a peak located at 280 nm. After 100 h of UV exposure, the pure PMMA sheet showed no differences in absorbance peak, whereas the absorption of lignin-PMMA became lower after the UV exposure, especially at the absorption peak (280 nm). These results indicated that lignin could be photo-degraded in the polymer blends under UV irradiation.

HSQC-NMR was performed to further investigate the lignin degradation and photocatalytic activity of ZnO nanoparticles. HSQC analysis allows us to analyze the abundance of chemical linkages in lignin polymer. In particular, β -aryl-ether (β -O-4) (Figure 2A) was the most abundant inter-linkage, representing the majority of the total lignin interlinkages in the lignin-PMMA blend (86.0%) the lignin-PMMA-ZnO blend (89.6%), respectively. The UV exposure had resulted in significant cleavage of β -O-4 linkages, as indicated by the much-decreased peak area of this linkage in HSQC (Figure 2A). More importantly, ZnO nanoparticle was found significantly promote the cleavage of lignin β -O-4 linkage under UV irradiation. As shown in Figure 2B, the frequency of β -O-4 linkage was only slightly decreased (16.2% decrement) when lignin-PMMA without ZnO was treated under UV; however, the frequency of β -O-4 linkage

was largely decreased (72.7% decrease) when the ZnO nanoparticles were added into the lignin-PMMA blend. In fact, most of the peak area for β -O-4 linkage in the HSQC for UV-treated lignin-PMMA-ZnO blend disappeared (Panel 3 of Figure 2B). These results highlighted that ZnO efficiently cleaved β -O-4 linkage in the lignin-PMMA-ZnO blend through photocatalysis.

The quantification of peak areas further confirmed the efficient lignin depolymerization catalyzed by ZnO in the polymer blend. As shown in Figure 2C, β -O-4 of lignin-PMMA after UV exposure decreased from 18.57 per 100 lignin benzene ring to 15.5, while β -O-4 in lignin-PMMA-ZnO decreased from 20.07 per 100 lignin benzene ring to 5.48 after the UV exposure. The quantified linkage profiles translated into a significant decrease (72.7%) of β -O-4 linkage in the lignin-PMMA-ZnO blend after UV exposure when compared to a minor decrease (16.2%) in lignin-PMMA blends. It was also notable that the frequency of phenylcoumaran (β -5) and resinol (β - β) linkage remained mostly unchanged after UV exposure, yet they also account for a much smaller portion of lignin interunit linkages (Figure S1 and Table S2). Overall, the highly efficient β -O-4 linkage cleavage by ZnO nanoparticles in the lignin-PMMA-ZnO blend proved to demonstrate the concept of phototunable plastic blends can be degraded efficiently at the end of service life.

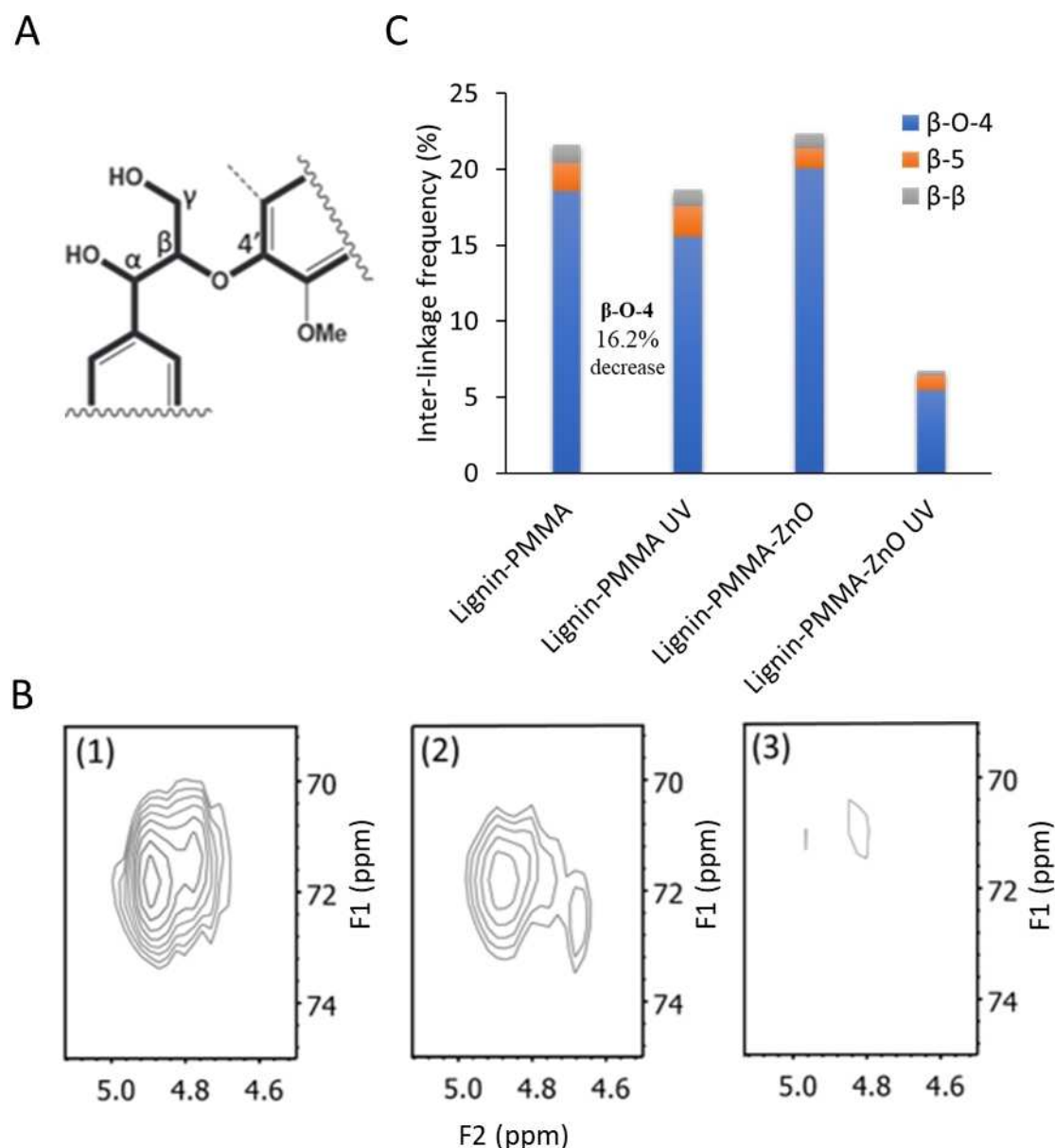


Figure 2. 2D HSQC spectra of β -O-4 linkage. (A) Chemical structure of β -O-4 linkage in lignin; β -O-4 linkage spectra of lignin derived from (B1) lignin-PMMA, (B2) lignin-PMMA UV, and (B3) lignin-PMMA-ZnO UV; (C) frequency of interunitary linkage integrated from 2D HSQC NMR. The complete NMR spectra of lignin linkages are in Figure S1.

Molecular mechanisms for efficient lignin depolymerization in the blend revealed by HSQC NMR

A detailed analysis of HSQC data revealed the mechanisms for efficient lignin depolymerization by ZnO nanoparticles in the polymer blends. Interestingly, the composition of monolignol changed significantly after UV exposure, in particular, the ZnO-containing polymer blend (Figure 3A, B, and C). The percentage of *p*-hydroxyphenyl (H) units in lignin from the lignin-PMMA blend was increased from 35.8% to 65.1% after UV exposure, while the percentage of H units in lignin-PMMA-ZnO blend increased from 46.5% to 85.4% after the UV exposure (Figure 3B). The percentages of both syringyl (S) and guaiacyl (G)

units were decreased after UV exposure, while the percentage of H unit was increased. The decrease of both S and G units for the lignin-PMMA-ZnO blend is more significant than those of lignin-PMMA.

The changes in monomer composition after UV exposure suggested that the G and S lignin were photo-degraded much more efficiently when compared to H lignin. This increased rapid degradation could be caused by both inter-linkage cleavage and ring-opening reactions of G and S lignin. Figure 3D showed the potential mechanisms for linkage cleavage and ring opening. For linkage cleavage, the hydroxyl radical $\cdot\text{OH}$ produced by ZnO nanoparticles will achieve the linkage cleavage (Figure 3D1). A similar hydroxyl radical could carry out

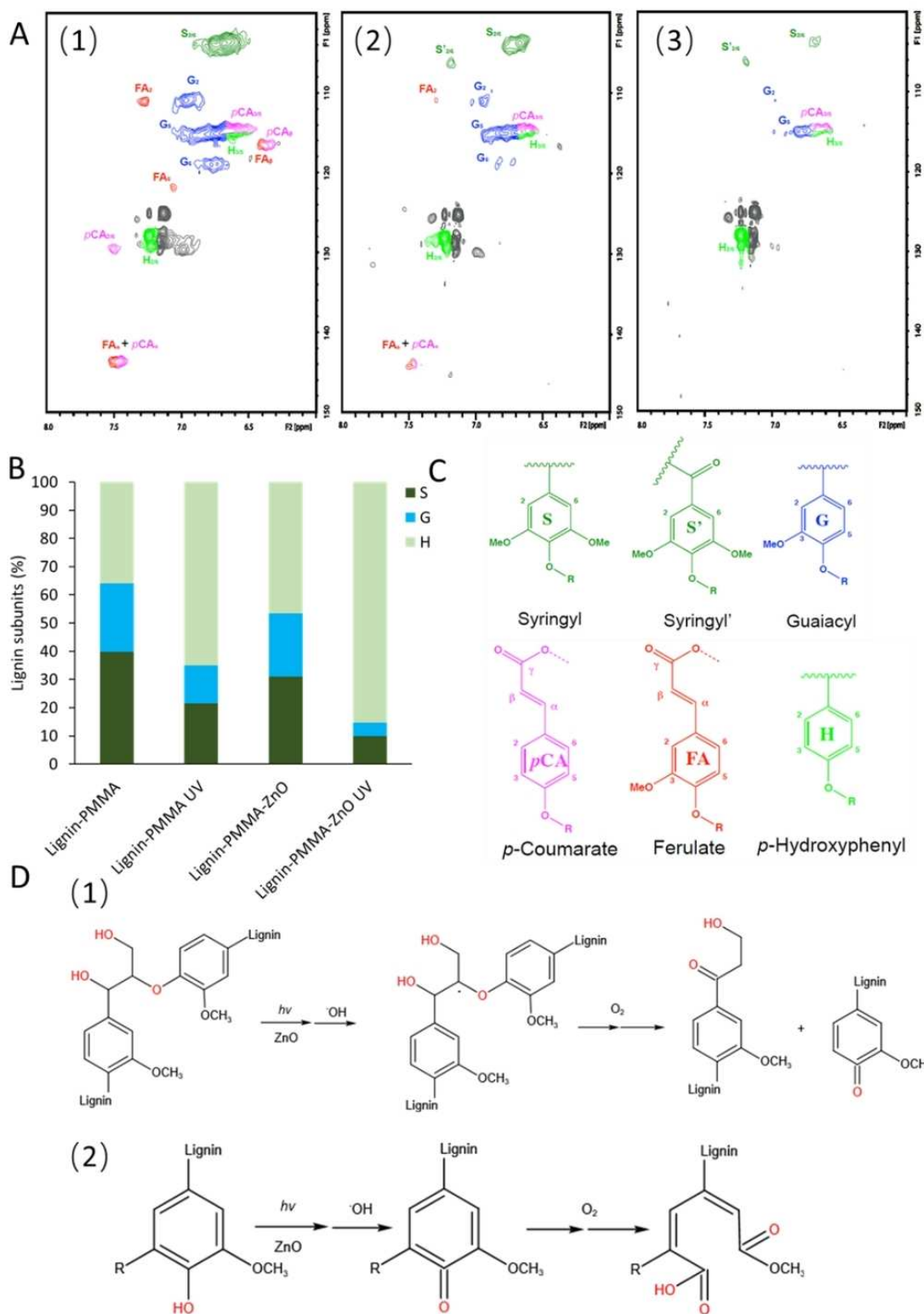


Figure 3. 2D HSQC spectra of the aromatic region of lignin. HSQC spectra of the aromatic region of (A1) lignin-PMMA, (A2) lignin-PMMA UV, (A3) lignin-PMMA-ZnO UV; B) calculated S/G/H ratio from HSQC; (C) chemical structures of aromatic moieties of lignin; potential degradation mechanism: (D1) β -O-4 linkage cleavage and (D2) ring-opening reaction.

the oxidation of methoxyl groups, which produced the intermediates for ring opening. Further oxidation could open

the rings for G and S lignin (Figure 3D2). The $-\text{OCH}_3$ decreasing was much less than those of G, and S lignin, indicating that the

–OCH₃ cleavage was not likely causing the degradation of the S and G lignin (Figure S1A). The S/G ratio remained at 1.6 after UV exposure for the lignin-PMMA blend. The S/G ratio was increased to 2.1 in the lignin-PMMA-ZnO blend after UV exposure (Table S2). The results indicate that G lignin could be more active in ZnO catalyzed photodegradation. Regardless of the detailed mechanisms, the HSQC data strongly support that ZnO catalyzed lignin degradation, which can be exploited for recycling or upcycling.

Enhancement of mechanical performances and recyclability of phototunable plastics

Even though phototunable lignin-based polymer blends represented a significant opportunity to develop recyclable plastics, the application of these new polymer blends depends on their properties, among which mechanical performances and recyclability are the most important ones. We, therefore, developed novel strategies to make our film with comparable performances with that of the commercial counterparts.

First, lignin and ZnO have been found to decrease the mechanical performance of the lignin-PMMA-ZnO blend. As shown in Figure 4A, PMMA film had an elastic modulus of 2.96 GPa and tensile strength of 66.9 MPa; however, both elastic modulus (2.74 GPa) and tensile strength (60.5 MPa) of lignin-PMMA film were lower than that of the PMMA film. Both elastic modulus and tensile strength were further decreased to 2.56 GPa and 43.6 MPa, respectively, for lignin-PMMA-ZnO that contained both lignin and ZnO. All these results suggested that the addition of both lignin and ZnO nanoparticles into the PMMA-based blend can reduce its mechanical properties.

Second, a plasticizer and a grafting polymerization strategy have been developed to enhance the mechanical performance of our blend film. To enhance the mechanical performance of lignin incorporated plastic blends, we first explored if plasticizers can improve the mechanical properties. We examined three plasticizers, namely indene,^[18] diethylene glycol dibenzoate (DEG-DB),^[18,19] and dioctyl phthalate (DOP).^[20] These plasticizers have been reported to improve the mechanical properties of blended materials. As shown in Figure 4B, only DOP slightly improved the elastic modulus of lignin-PMMA, but its tensile strength remained to be much lower than that of PMMA. Moreover, we did not find any enhancement of both indene and DEG-DB to the mechanical performance of the lignin-PMMA blends (Figure 4B). These results indicated that the plasticizers were not functional as the mechanical enforcement, which could be attributed to the poor interaction between lignin and the polymer matrix and the remained domain size of lignin in the polymer matrix. Both lignin-polymer interaction and lignin domain size could not be improved by the added plasticizers.

Another grafting polymerization strategy was thus further developed to address the mechanical performance of our blend film. Instead of blending lignin with PMMA and using the plasticizers, we synthesized PMMA-*g*-lignin grafted polymer using lignin as the molecular core, MMA as the growing chain,

and azobisisobutyronitrile (AIBN) as the initiator. After MMA grafting to lignin, it continued to be polymerized into PMMA, which was interconnected by lignin. With this structural design, lignin-polymer interaction could be much enhanced, and lignin domains could be well distributed in the polymer matrix. As shown in Figure 4C1, the resultant PMMA-*g*-lignin sheet had excellent uniformity, indicated good compatibility of polymers and their enhanced interactions. In fact, the elastic modulus of PMMA-*g*-lignin reached 3.20 GPa, which was even higher than that of commercial PMMA (2.96 GPa) (Figure 4C3). The tensile strength of this PMMA-*g*-lignin (59.1 MPa) was comparable to that of the commercial PMMA film (Figure 4C3). Different from the lignin-PMMA-ZnO blend, the addition of ZnO nanoparticles into PMMA-*g*-lignin (PMMA-*g*-lignin-ZnO) did not lead to significant decreases in both elastic modulus and tensile strength (Table S3). In particular, the elastic modulus of PMMA-*g*-lignin-ZnO (3.15 GPa) was significantly higher than that of PMMA, and the tensile strength (64.2 MPa) kept very slightly changed (Table S3). As compared with other reported lignin and PMMA blends, our PMMA-*g*-lignin blend had superior mechanical property, especially its elastic modulus represents the highest one.^[9,12] All these results highlighted that grafting polymerization has efficiently addressed the challenge of mechanical property for our lignin-PMMA blend.

More importantly, after UV treatment, the elastic modulus (2.45 GPa) and tensile strength (52.5 MPa) of the PMMA-*g*-lignin polymer blend dropped significantly, respectively. This significant decrease was different from the UV-treated lignin-PMMA, which lead to barely any changes in mechanical properties. The decrease in elastic modulus and tensile strength indicated that the aforementioned interlinkage cleavage and ring-opening could break down the lignin core in the new design, freeing PMMA chains from the lignin core. The weakened mechanical performance could allow for lower energy in the processing to enable better recyclability.

Third, in addition to the mechanical properties, we evaluated the abovementioned recyclability of our PMMA-*g*-lignin. Ideally, the depolymerization of lignin molecule could separate the compositional polymers in the polymer blends, allowing the PMMA to be recycled. In this process, we first treated PMMA-*g*-lignin with 100 h of UV exposure for ring opening and cleavage, and then UV treated blend (211.3 mg) was dissolved with an alkaline isopropanol solution. After the treatment, the ether bond between PMMA chains and degraded lignin core was hydrolyzed, which enabled the extraction of lignin thereafter by adjusting pH to neutral and then adding chloroform (Figure 4D). PMMA (148.4 mg) and lignin (15.1 mg) were recycled at a reasonable yield (77.4%). The molecular weight of the recycled lignin was further characterized by gel permeation chromatography (GPC), which was much lower ($M_n = 137 \text{ g mol}^{-1}$ and $M_w = 229 \text{ g mol}^{-1}$) than those of the raw lignin used for grafting polymerization ($M_n = 2726 \text{ g mol}^{-1}$, $M_w = 1079 \text{ g mol}^{-1}$). This result suggested that the lignin core in the PMMA-*g*-lignin blend has been degraded. The GPC data displayed that the PMMA extracted from PMMA-*g*-lignin UV through this recycling process had higher M_n (52197 g mol^{-1}) and M_w (88089 g mol^{-1}) than that of commercial

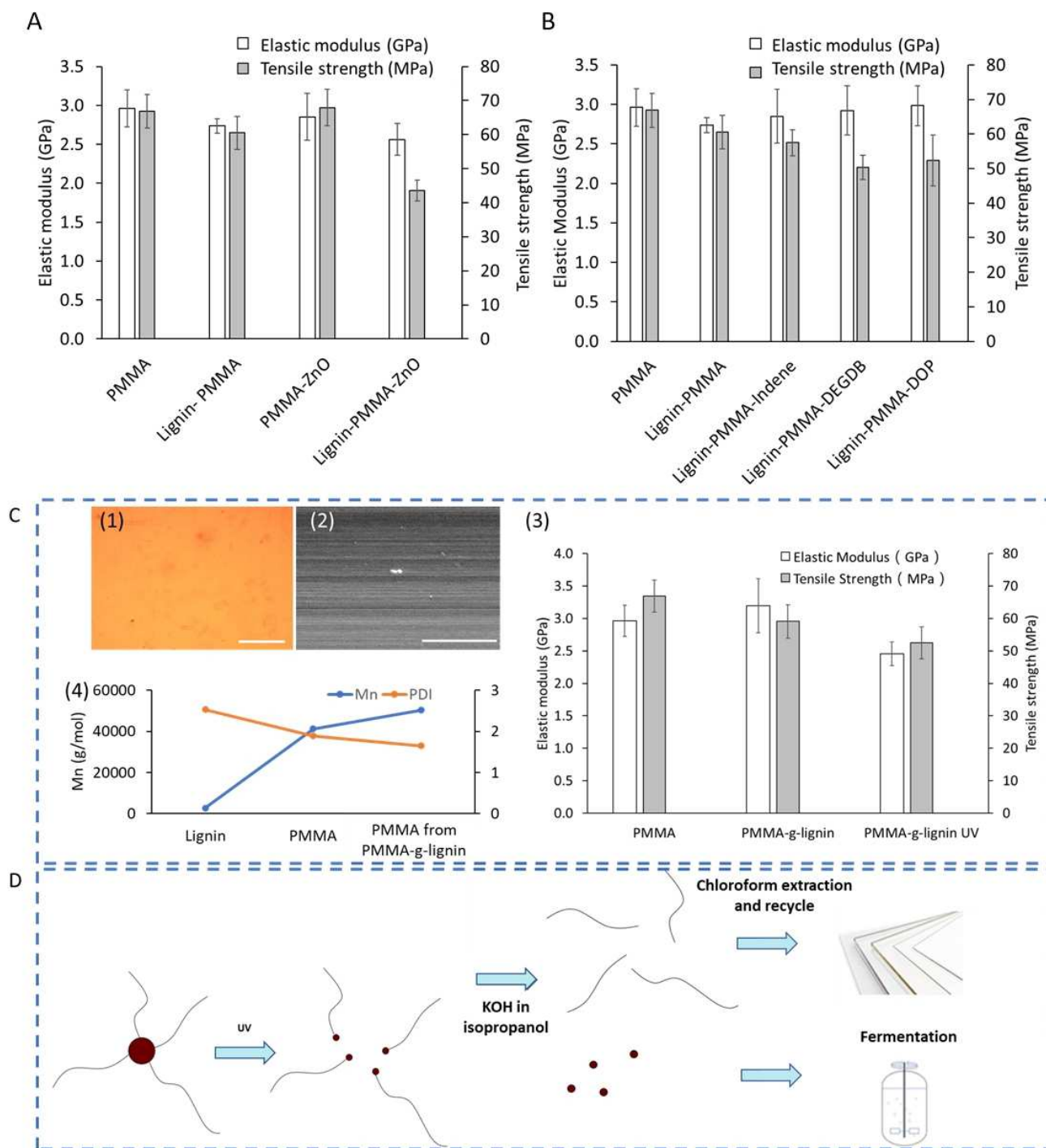


Figure 4. Enhancement of performances of lignin-PMMA blend and recycle process design. (A) Values of elastic modulus and tensile strength of lignin-PMMA blend samples. (B) Values of elastic modulus and tensile strength of lignin blend with various plasticizers, DEGDB is the abbreviation for diethylene glycol dibenzoate, DOP is the abbreviation for dioctyl phthalate. Graft-polymerization samples: (C1) Optical microscope image of PMMA-g-lignin; (C2) SEM image of PMMA-g-lignin (all scale bars are 50 μm); (C3) elastic modulus and tensile strength of commercial PMMA, PMMA-g-lignin, and PMMA-g-lignin UV; (C4) molecular weight and PDI of the lignin, commercial PMMA, and PMMA chains cleaved from PMMA-g-lignin. (D) Recycle strategy of the graft polymerization sheet.

PMMA. The PDI as the molecular uniformity for the PMMA extracted from the PMMA-g-lignin was 1.65, which is smaller than that of the commercial PMMA 1.89 (Figure 4C4). In the meantime, the recycled PMMA has good film processability. The

resultant film made of the recycled PMMA has good mechanical performance (2.75 GPa elastic modulus and 45.2 MPa tensile strength, Table S3), which was comparable with the raw PMMA film.

Molecular designs by using grafting polymerization can simultaneously enhance the mechanical properties and recyclability of blends, where the underlying mechanism could lie in the enhanced molecular interactions. Our initial analysis indicated that the mechanical properties of the lignin-PMMA and lignin-PMMA-ZnO after UV treatment were not significantly different (Table S1). The results revealed a steeper challenge in that if the lignin and PMMA existing as a blend and were not chemically linked, the photodegradation of lignin did not necessarily lead to better recyclability of the lignin-based blend. Even though lignin can be efficiently photo-degraded by ZnO nanoparticles, lignin might form small particles in the PMMA blend, with some ZnO nanoparticles encased in them. Although water absorption of the thin sheet was enhanced by the lignin addition, the hydroxyl radicals produced by ZnO under UV irradiation had extremely restricted mobility in the blend. This limited both the photodegradation effectiveness and the recyclability, as the partially degraded lignin particles could affect the PMMA structure surrounding them. Such limitation was also reflected by the fact that UV treatment has very little impact on the overall mechanical property of the lignin-PMMA-ZnO blend, even though most of the lignin interunit linkages were cleaved. Such limitation had been mitigated by grafting polymerization, which can form abundant chemical bonds in the resultant PMMA-*g*-lignin, which contains immediately interacted PMMA and lignin polymers. Even without the addition of ZnO, the mechanical performance of PMMA-*g*-lignin had been significantly decreased after UV irradiation (Figure 4C3), suggested that even slightly breaking down the lignin core in the PMMA-*g*-lignin block can induce the separation of lignin and PMMA polymers, which thus enable the excellent recyclability.

Here we propose that the recycled PMMA could be upcycled for blend fabrication; meanwhile, the depolymerized lignin that enabled the PMMA upcycling could also be upcycled as a suitable substrate for bacterial fermentation to produce other types of biodegradable bioplastics like polyhydroxyalkanoate (PHA)^[12b,21] and other value-added products such as lipid^[12a] and asphalt binder modifier.^[15b] The rationale of these proposed applications was based on previous studies that lignin with small molecular weight was more suitable than the high molecular weight lignin for bioconversion by *Pseudomonas putida* fermentation for PHA production,^[12b,22] *Rhodococcus opacus* fermentation for lipid production^[12a] and as a superior asphalt binder modifier to enhance the asphalt binder temperature performance.^[15b] The great upcycling potential along with the good mechanical performance of our PMMA-*g*-lignin thereby can be an excellent plastic alternative to tackle current environmental challenges associated with the massive utilization of synthetic plastics.

New phototunable lignin-based polymer blends offer a new opportunity for recyclable and renewable plastics

The mechanical properties and recyclability of the novel design of PMMA-*g*-lignin-ZnO system opened up new avenues to

address the challenges of handling the conventional petrochemical plastics wastes. First, the new strategy exploited a cost-effective, abundant, and renewable polymer, lignin to mix blend with petrochemical plastics. The unique photodegradable capacity of lignin could be used to efficiently break down the lignin structure, due to its unique material design, where lignin was at the core of the polymer network. Once these grafting points were dissociated, the entire polymer network began to dissociate. The unique lignin degradation mechanisms enabled a novel recycling strategy. The utilization of degradable biopolymer to design a similar polymer with controlled and increased recyclability could derive a variety of different types of renewable polymeric systems for broad applications. Second, lignin was known to contain abundant functional groups, allowing chemical linkages to be built with many kinds of polymers. Similar lignin-based polymeric systems could be prepared with various petrochemical polymers including PE, PP, PET and others. Third, the utilization of lignin waste stream for lignocellulosic biorefinery could improve both sustainability and cost-effectiveness of lignocellulosic biofuel. Overall, the new blend design could address multiple environmental challenges from non-degradable plastics to renewable fuels and products.

Conclusions

In this study, we have demonstrated the concept of phototunable and renewable plastics that leverage the photodegradability of lignin. The UV exposure of the lignin-PMMA-ZnO blend highlighted the rapid degradation by ZnO catalysts, as indicated by the efficient cleavage of the β -O-4 bond. The compromised mechanical properties and recyclability have been solved by designing a new PMMA-*g*-lignin-ZnO system, possessing enhanced properties compared to PMMA, enabling a recycling process combined with phototreatment using solution-based separation. The new blend and process could have broader applications in recyclable plastics.

Experimental Section

Materials

Commercial PMMA pellets were from Kaneka Americas holding, Inc. Corn stover was harvested in the Texas A&M University Farm and oven-dried (70 °C). Chemicals were purchased from Sigma Aldrich.

Isolation of lignin

Lignin was prepared from the corn stover following the published method.^[16] In brief, 50 g of corn stover was loaded at 10% (*w/w*) solid loading using liquid hot water, then pretreatment heated by an Amsco LG 250 Laboratory Steam Sterilizer (Steris, USA) (121 °C, 30 min). After filtration, the solid fraction was pretreated using 50% ethanol and 1% NaOH (121 °C, 1 h). The liquid stream containing lignin was collected for precipitation. 100 mL of liquid stream was titrated to pH_2 HCl solution (1 L) and stirred for 1 h. Lignin precipitates were separated by centrifugation. Lignin precipitates

were washed using a pH_2 HCl solution three times and de-ionized water for one more time. Lignin precipitates were further dried using a FreeZone 4.5 Liter Benchtop lyophilizer (MO, USA)

Preparation of ZnO nanoparticles

Colloidal ZnO nanoparticles were prepared by hydrolyzing zinc acetate dihydrate in the basic methanol solution following the published method.^[23]

Briefly, KOH (16 mmol) was dissolved in methanol (150 mL) at 60 °C and stirred for 30 min. 50 mL of zinc acetate dihydrate methanol solution (0.16 M) was added into the potassium hydroxide solution at 60 °C and stirred for 2 h. Hexane and isopropanol were added into the ZnO nanoparticles methanol solution with a volume ratio of 5:1:1. After the mix was kept at 0 °C overnight, ZnO precipitate was separated using centrifugation. The ZnO precipitate was washed using methanol three times and redispersed in a methanol and hexane mix (volume ratio of 3:1).

Preparation of lignin-PMMA and lignin-PMMA-ZnO blends

Commercial PMMA pellets (4.5 g) were added to *N,N*-dimethyl formamide (DMF) (10 mL), and stirred at 60 °C for 1 h. For the PMMA-ZnO blend, ZnO nanoparticles solution (58 μ L) was added. For the lignin-PMMA blend, lignin powder (0.5 g) was added, and stirred at 60 °C for an additional 1 h. For the lignin-PMMA-ZnO blend, add lignin powder and stir at 60 °C for 1 h. ZnO nanoparticles solution (58 μ L) was added and stirred at 60 °C for 1 h. All samples were dried in a vacuum oven for 24 h in aluminum plates. Dried samples were cut and hot pressed under 150 °C.

Optical microscope

The blend sheets were placed on cover glasses, then directly observed using an Olympus BX60 optical microscope (OM) in transmission mode. The total magnification was 50X.

UV exposure

Two 100W PHILIPS TL 100W/10R tubes were placed 10 cm above the sample sheets in a closed cabin. UV exposure time was 100 h.

UV/Vis absorption spectra

The absorption spectra were measured using an Epoch Biotek Microplate Spectrophotometer in spectral scanning mode, from 200 nm to 500 nm.

SEM and element mapping

Scanning electron microscopy (SEM) images were recorded on a Tescan FERA-3 Model GMH Focused Ion Beam Microscope at an accelerating voltage of 5 kV. Atom number and element weight ratio for major elements such as C, O, and Zn of samples were measured by energy dispersive spectroscopy (EDS).

Tensile testing

The sheets were cut into strip-like sharp, with the dimension of about 1.5 mm in width and 4 cm in length. The precise width and thickness were measured using a Vernier caliper and a Spiral

micrometer, respectively. RSA 3 dynamic mechanical analyzer (TA instruments, DE, US) was used to measure mechanical properties.

NMR analysis of lignin

300 mg of lignin-PMMA blend sheet was cut and dissolved in 6 mL of toluene. After dissolution, the sample was centrifuged, and then the supernatant was discarded. The lignin precipitates were washed using toluene and centrifuged again. After that, the lignin was dried in a vacuum oven. Lignin was dissolved in $[D_6]$ DMSO (0.6 mL) and then transferred in an NMR tube. Lignin samples were characterized by a 2D HSQC NMR Bruker AVANCE 500 MHz spectrometer that was equipped with a cryoprobe as reported before.^[13c] The obtained HSQC spectra was analyzed using the MestReNova software.

Preparation of PMMA-*g*-lignin blend sheet

Lignin (0.2 g) and glycidyl methacrylate (GMA) (0.4 g) was dissolved in 50 mL of DMF, and the reaction was carried at 80 °C in an N_2 atmosphere for 24 h. After the reaction, methanol was added to precipitate the lignin-GMA out. The precipitation was separated by centrifugation and washed with methanol three times. Precipitation was weighted and 35 times methyl methacrylate (MMA) by weight, and 0.165 times azobisisobutyronitrile (AIBN) was added to lignin-GMA. The reaction was carried out at 60 °C in an N_2 atmosphere for 24 h. PMMA-*g*-lignin was precipitated by adding three times toluene by volume and separated by centrifugation. The precipitation was washed with toluene three times. The sample was dried in a vacuum oven for 24 h, and hot pressed at 150 °C.

Gel permeation chromatography

The molecular weights of lignin were measured by a gel permeation chromatographic (HLC-8320 Eco SEC Elite GPC system, Tosoh Bioscience LLC, CA, USA). The PMMA cleaved from PMMA-*g*-lignin was isolated using a modified method.^[24] The PMMA-*g*-lignin sheet was added into a saturated KOH isopropanol solution and stirred overnight. After reaction, neutralizing using hydrochloric acid (0.1 M). The cleaved PMMA was extracted with chloroform. Lignin and commercial PMMA samples were dissolved in chloroform before characterizing with GPC.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: lignin · photocatalytic depolymerization · plastic recyclability · polymethyl methacrylate · zinc oxide

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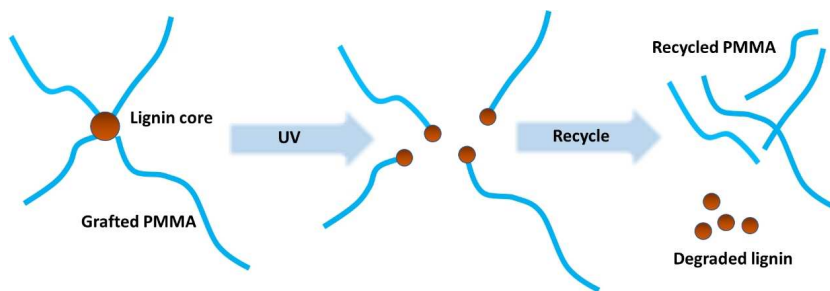
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FULL PAPERS



Lignin-enabled phototunable recycling of plastics: A PMMA-*g*-lignin-ZnO polymeric film with superior mechanical performance has been developed, where photo-de-

gradable lignin serves as core to be cleaved by ZnO nanocatalysts and to enable the recycling of PMMA after UV irradiation.

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Phototunable Lignin Plastics to Enable Recyclability

