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Thermo-Mechanical Properties of Polypropylene Blends with Esterified Lignin

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Abstract: Lignin, a renewable and widely available biopolymer, has been explored as an additive in polyolefins to develop high value-added materials. However, its low compatibility with polymers like polypropylene (PP) often causes poor particle dispersion and compromised mechanical properties. Esterification has proven effective in enhancing lignin-polyolefin interactions. This study evaluated the incorporation of kraft lignin (KL) and maleic anhydride-modified kraft lignin (MAKL) into PP, focusing on lignin dispersion and the blends' thermal, mechanical, and viscoelastic properties. Thermal analyses showed that MAKL reduced PP crystallinity, indicating improved compatibility, supported by micrographs showing more uniform particle dispersion. Mechanically, low MAKL concentrations maintained yield strength similar to neat PP, while 5 wt% MAKL increased impact strength by up to 148%. This improvement was attributed to enhanced interfacial interaction, reduced crystallinity, and better energy dissipation. The findings demonstrate that esterification of lignin with maleic anhydride effectively overcomes compatibility limitations with PP, leading to significant gains in mechanical and viscoelastic properties. This work advances lignin's sustainable use in polymer blends, emphasizing its potential as a renewable alternative in material development.

Keywords: kraft lignin; esterification; polypropylene; mechanical properties; viscoelastic properties

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1. Introduction

Lignin is the second most abundant biopolymer on Earth, after cellulose, and is found in the cell walls of plants and trees. It plays a crucial role by providing rigidity and mechanical support to plant tissues [1–3]. It is an amorphous aromatic macromolecule composed of phenylpropanoid units—p-hydroxyphenyl, syringyl, and guaiacyl—organized in a complex three-dimensional structure [4–6]. Furthermore, lignin features several functional groups, with aliphatic and phenolic hydroxyl groups being particularly prominent [7,8].

Among the various technical lignins, kraft lignin, a product of the pulping process in the paper and pulp industry, is the most readily available, with an annual production estimated at 130 million tons [4,9,10]. While historically treated as a low-value byproduct primarily used for thermal energy generation [11], lignin has increasingly been explored for its potential in high-value applications [2,10,12]. In particular, its incorporation into polymer matrices has garnered significant attention due to reported improvements in mechanical stiffness [13,14], electrical properties [9], adhesion [3,15,16], antioxidant activity [17,18], and flame retardancy [19]. Additionally, blending lignin with commercial fossil-based polymers can contribute to reducing greenhouse gas emissions and offers advantages such as low cost and abrasiveness [20,21].

However, a major limitation to the large-scale use of lignin is its poor dispersion within polymer matrices, which stems from its inherent chemical structure. Lignin exhibits a strong tendency to form agglomerates due to interactions between its functional groups, while its complex structure limits solubility and hinders uniform dispersion [9,20]. Although processing-induced shear forces can fragment lignin into smaller particles, this effect is counterbalanced by particle coalescence, especially at higher lignin concentrations [20]. This challenge is particularly pronounced in non-polar matrices such as polypropylene (PP), which exhibits poor compatibility with lignin due to their low structural affinity [13,20].

Polypropylene, on the other hand, is widely used in industrial applications due to its low cost, excellent mechanical properties, and ease of processing [16,21]. Consequently, several studies have investigated PP-lignin blends. Despite the inherent incompatibility between these materials, even small lignin additions have demonstrated significant functional improvements in PP, including modifications to its surface free energy [16] and stabilization effect [18]. Nevertheless, higher lignin concentrations often lead to deteriorated mechanical properties, limiting its applicability in such blends [13–15,20,22].

A promising strategy to address these limitations is the chemical modification of lignin. The hydroxyl groups in lignin's structure are highly reactive, enabling the introduction of chemical groups that modify its polar character and enhance its solubility in non-polar matrices [1,23]. Among the available modification methods, alkylation and esterification reactions have been extensively studied, with the latter showing greater efficacy in improving lignin's compatibility with polymers such as PP [22,23]. Maldhure et al. [22] conducted a comparative study on PP blends containing lignin esterified with maleic anhydride or alkylated with dichloroethane at concentrations ranging from 5 to 25 wt%. Morphological analyses demonstrated enhanced interaction, solubility, and dispersion of the esterified lignin in the PP matrix, attributed to the increased aliphatic content in the lignin structure. Mechanical testing revealed that the blends with esterified lignin retained mechanical properties comparable to pure PP up to a concentration of 10 wt%, with only a slight decline observed at higher lignin concentrations. Similarly, Orebom et al. [24] investigated the esterification of lignin with fatty acids, incorporating 20 wt% of the modified lignin into various polymer matrices, including PP. While the inclusion of esterified lignin reduced the mechanical properties overall, the values obtained for the PP matrix remained close to those of the unmodified polymer. Remarkably, the impact resistance of the PP-lignin blend reached 93% of that of pure PP, indicating favorable interactions between the components. Furthermore, Dehne et al. [25] studied the effects of lignin source and esterification, performed using acetic, propionic, and butyric anhydrides, in blends with high-density polyethylene (HDPE), a non-polar polymer, at a 1:1 weight ratio. Their findings revealed that, compared to unmodified lignin, esterified lignin significantly improved elongation at break and tensile strength. These improvements became more pronounced as the carbon chain length of the esterifying agents increased.

Despite these advances in lignin modification for better interaction with nonpolar polymers, further investigation is still required to achieve a deeper understanding of the factors involved in this interaction. Therefore, this study aims to analyze the interaction between modified lignin and PP, focusing on the viscoelastic behavior and morphological effects of these materials and their influence on the final properties of the resulting composites. To achieve this, kraft lignin was modified using a simplified esterification route by reacting with maleic anhydride. The results demonstrate that this modification enhances the dispersion of lignin in PP, improving not only its mechanical properties but also its viscoelastic behavior. By focusing on the critical role of particle dispersion and interfacial interactions, this study offers valuable insights into the effective integration of lignin into PP, contributing to the development of sustainable materials with enhanced performance characteristics.

2. Materials and Methods

2.1. Materials

A development-grade kraft lignin (KL) from eucalyptus (hardwood) was kindly provided by Suzano S.A. (Limeira, Brazil). The KL is in a solid (powder) state, brown in color, with a pH of 8.1. Maleic anhydride (analytical grade) used for the esterification of KL was purchased from Merck (Diadema, Brazil). Acetone (analytical grade) and silicone oil were also obtained from Merck (Diadema, Brazil). The isotactic polypropylene (iPP) used was supplied by Petroquímica CUYO S.A.I.C. (Buenos Aires, Argentina), with a density ranging between 0.88 and 0.92 g cm^{-3}.

2.2. Modification of Kraft Lignin

The modification of kraft lignin (KL), based on the method described by Chen et al. [26], involved adding 150 g of KL, pre-dried at 70 °C for 24 h, to a 10% maleic anhydride solution in acetone at a 1:20 (w/v) ratio in a round-bottom flask. The flask was immersed in a silicone oil bath maintained at 60 °C. Once the temperature stabilized, the mixture was magnetically stirred under reflux for 7 h. Figure 1 illustrates the esterification reaction of kraft lignin with maleic anhydride. Upon completion of the reaction, acetone was evaporated, and deionized water was added to precipitate the product. The precipitate was washed with distilled water at least five times, vacuum-filtered, and dried at 80 °C for 24 h. The dried product was subsequently ground into a fine black powder. The final product is called MAKL.

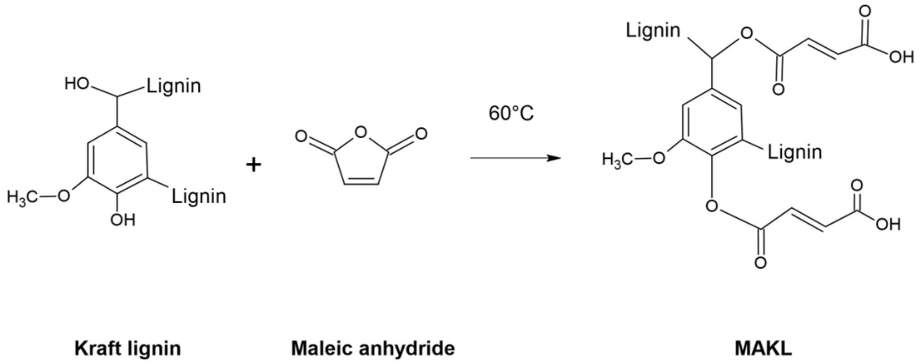

Figure 1. Chemical modification reaction of lignin using maleic anhydride.

2.3. Polymer Processing

The preparation of PP blends incorporating KL or MAKL was conducted via melt extrusion using a co-rotating twin-screw extruder, Coperion ZSK 18 (Stuttgart, Germany). The extrusion process was performed at a screw speed of 450 rpm, with the temperature set between 160 °C and 210 °C across nine distinct zones, spanning from the feed section to the die. The lignin content in the blends varied between 2.5 wt% and 10 wt%, as detailed in Table 1.

Table 1. Sample nomenclature and compositions.

Sample	PP (wt%)	KL (wt%)	MAKL (wt%)
PP	100	0	0
PP-KL 2.5	97.5	2.5	0
PP-KL 5.0	95.0	5.0	0
PP-KL 10.0	90.0	10.0	0
PP-MAKL 2.5	97.5	0	2.5
PP-MAKL 5.0	95.0	0	5.0
PP-MAKL 10.0	90.0	0	10.0

The specimens were prepared using a molten-state injection molding process with a Micro Injector, Xplore IM12 (Sittard, The Netherlands). The injection molding was conducted at 210 °C, with an injection pressure of 6 bar and a total cycle time of 30 s. Tensile test specimens were prepared in accordance with ISO 527-2 [27] Type 1 BA, while impact test specimens were prepared following ASTM D256-23e1 [28] standards. Dynamic mechanical analysis (DMA) was performed on the same specimens used for the impact tests.

2.4. Lignin Characterizations

Fourier Transform Infrared Spectroscopy in Attenuated Total Reflectance mode (FTIR-ATR) was used to confirm the modification of kraft lignin (KL) into maleic anhydride-modified kraft lignin (MAKL). Characterization was performed using a Spectrum Two instrument, PerkinElmer (Hopkinton, MA, USA). Spectra were acquired from 4000 to 500 cm^{-1}, with 32 scans and a resolution of 4 cm^{-1}. The obtained spectra were normalized relative to the peak of the aromatic ring at 1514 cm^{-1}.

Differential scanning calorimetry (DSC) analysis was conducted using a DSC, TA Instruments Q200 (Waltham, MA, USA). Approximately 8 mg of each sample was weighed. The procedure involved heating the sample from 25 °C to 200 °C, holding it isothermally for 3 min to erase thermal history, followed by cooling to 25 °C and a second heating to 200 °C. All heating and cooling cycles were performed at a rate of 10 °C min^{-1} under an inert nitrogen atmosphere. The glass transition temperature (T_g) of the samples was determined during the second heating cycle.

2.5. Polymer Characterizations

Optical microscopy was used to evaluate the dispersion of KL and MAKL within the PP matrix. Micrographs were captured using a microscope, Carl Zeiss Axio Scope A1 (Oberkochen, Germany), equipped with a heating module, Linkam T95 HS (Salfords, UK). For sample preparation, approximately 4 mg of each sample was placed on a glass slide, covered with a coverslip, and heated to 210 °C before being gently compressed with tweezers. After cooling to room temperature, the samples were analyzed to obtain images of the lignin dispersion.

DSC analysis was conducted using a DSC, TA Instruments Q200 (Waltham, MA, USA). Approximately 10 mg of each sample was heated to 210 °C at a rate of 10 °C min^{-1}, held isothermally for 5 min to erase thermal history, then cooled to −25 °C and reheated to 210 °C. All cycles were performed under an inert nitrogen atmosphere. The melting temperature (T_m) was extracted from the second heating curve, while the crystallization temperature (T_c) was determined from the cooling curve. The effect of lignin incorporation on the crystallinity of the PP phase was evaluated by calculating the degree of crystallinity (X_c) using Equation (1):

$$X_c = \frac{\Delta H_m}{\Delta H_m^0 \times f} \times 100, \tag{1}$$

where ΔH_m represents the measured enthalpy of fusion for the sample, ΔH_m^0 corresponds to the enthalpy of fusion for fully crystalline polypropylene (207 J g^{-1}) [15], and f denotes the polypropylene fraction.

DMA was performed using a DMA, TA Instruments Q800 (Waltham, MA, USA) to assess the variation in the viscoelastic properties of PP with the addition of KL or MAKL. Samples were analyzed in single cantilever mode at a frequency of 1 Hz and a strain amplitude of 15 µM. The testing temperature ranged from −40 °C to 120 °C, with a heating rate of 5 °C min^{-1}.

The mechanical properties of the samples were evaluated through tensile and Izod impact strength tests. Tensile tests were conducted using an universal testing machine, Instron 3369 (Norwood, MA, USA), equipped with a 50 kN load cell, operating at a displacement rate of 5 mm min^{-1}. Izod impact strength tests on notched samples were performed using an equipment Shanta Engineering (Dhokali, India) with a pendulum of nominal energy capacity of 5.42 J. Five specimens were analyzed for each condition.

3. Results and Discussion

3.1. Lignin Modification

Figure 2 displays the FTIR spectra of KL and MAKL. A comparison of the spectra highlights changes that are consistent with the chemical modification of lignin. In particular, an increase in the intensity of the peaks at 1715 cm^{-1}, corresponding to the carbonyl group, and at 1210 cm^{-1}, attributed to the C–O stretching vibration [29], was observed. These spectral changes suggest a successful esterification reaction between lignin and maleic anhydride, as evidenced by the enhanced intensity of ester and carboxyl group bands [22,26,29]. Furthermore, the increased intensity of bands within the 3050–2800 cm^{-1} region, associated with the symmetric and asymmetric stretching of CH_2 and CH_3 groups, provides additional confirmation of the modification process [15,29]. Finally, the prevalence of hydroxyl groups in the MAKL spectrum, identified in the broad shoulder within the 3700–3050 cm^{-1} region, characterizes a partial esterification of lignin.

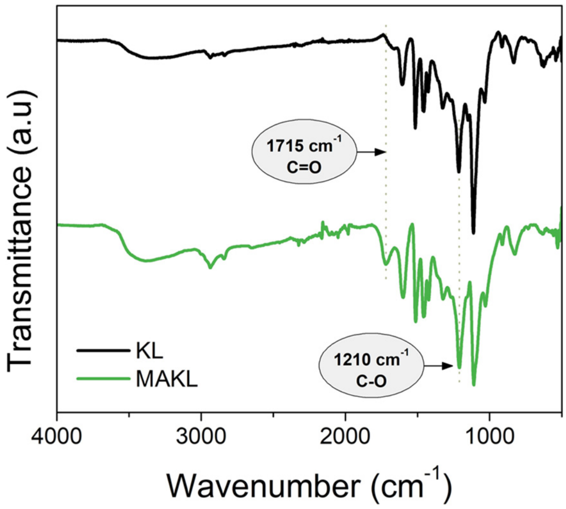

Figure 2. FTIR spectra of KL and MAKL.

Figure 3 displays the DSC curves of the lignins. Consistent with the FTIR findings, thermal analysis was performed to further evaluate the modifications of KL. The T_g of KL was determined to be 165 °C, aligning with the range reported in the literature for this material [1,30]. Following esterification, MAKL exhibited a slightly reduced T_g of 158 °C. This decrease is a well-documented phenomenon in the literature for lignin subjected to various chemical modification routes [15,29,31,32] and is attributed to the increased free molecular volume resulting from the addition of lateral groups to the polymer chain [29]. These results confirm the successful chemical modification of KL through esterification.

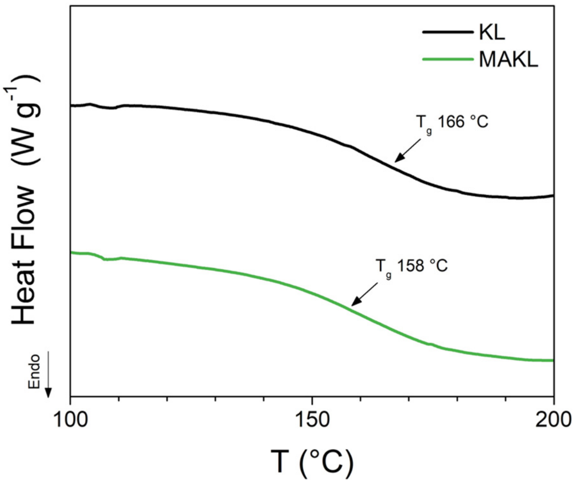

Figure 3. DSC thermograms of KL and MAKL.

3.2. Dispersion of Lignin

Figure 4 presents micrographs of the PP-KL (Figure 4a–c) and PP-MAKL (Figure 4d–f) samples.

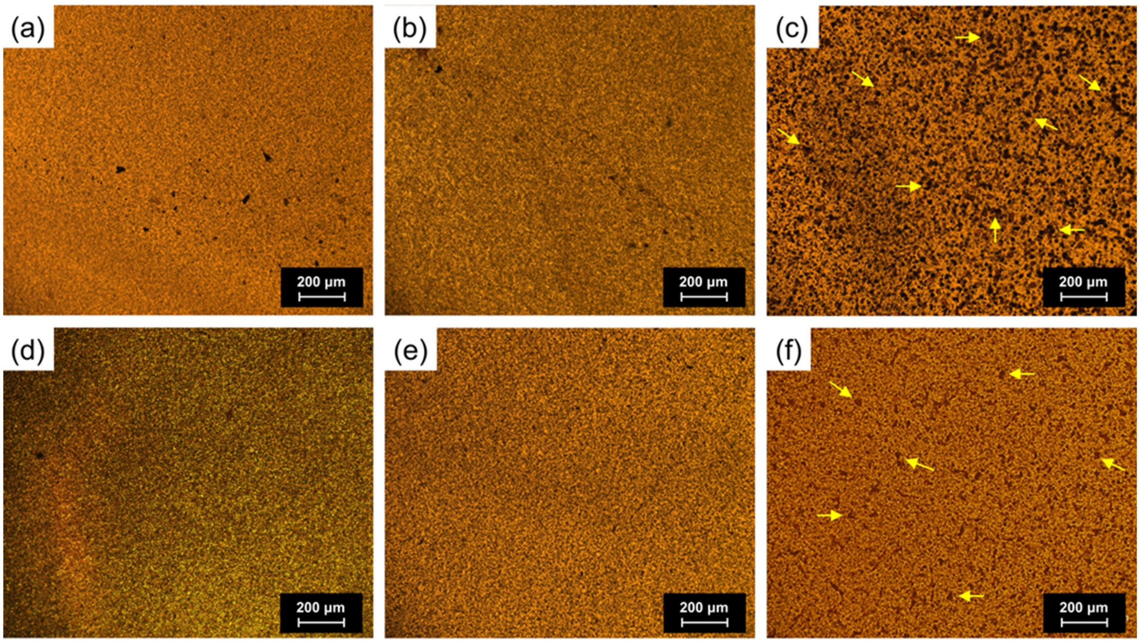

Figure 4. Optical micrographs of PP with lignin: concentrations of 2.5, 5.0, and 10.0 wt% of KL (**a**–**c**) and MAKL (**d**–**f**). Yellow arrows highlight some pronounced aggregation.

The optical micrographs reveal clear differences in dispersion between the blends containing unmodified KL and those with MAKL. In the unmodified KL blends, larger and more unevenly distributed particles are observed, whereas the MAKL-based blends show a more homogeneous dispersion, with smaller and more uniformly distributed particles. This improvement in dispersion is particularly evident in the blends with 2.5 and 5 wt% MAKL. However, at a concentration of 10 wt%, both KL and MAKL-based blends exhibit severe phase separation, with larger particles and more pronounced aggregation (indicated by yellow arrows). Despite these variations, all blends remain immiscible, with clear phase separation between the PP and lignin components.

Maldhure et al. [22] evaluated the modification of lignin using two routes: one with maleic anhydride and the other with dichloroethane and anhydrous aluminum chloride. Both modifications significantly enhanced the dispersion of lignin particles in the PP blend, reducing particle size and improving the homogeneity between the lignin and PP phases. However, the lignin modified with maleic anhydride demonstrated superior dispersion and mechanical properties compared to the lignin modified with dichloroethane. The modified lignins improved dispersion and particle size, particularly when up to 10 wt% modified lignin was used.

Although PP and MAKL remain immiscible, maleic anhydride modification strengthens interphase adhesion, resulting in a more uniform distribution of MAKL particles and consequently improved blend properties [20,33,34]. The esterification of lignin with maleic anhydride improves its compatibility with PP by grafting aliphatic chains onto the lignin surface. These chains extend the molecular structure of lignin, facilitating intermolecular interactions with the non-polar PP matrix. This modification contributes to a more uniform dispersion of lignin within the polymeric matrix and reduces particle aggregation [25].

3.3. Thermal Properties

DSC analysis was performed to assess the impact of the addition of KL or MAKL on the thermal properties of the PP matrix. Table 2 summarizes the thermal events of neat PP and its blends based on KL or MAKL, including the melting temperature (T_m) crystallization temperature (T_c), and degree of crystallinity (X_c).

Table 2. Main thermal parameters obtained from DSC analysis. T_m is the melting peak temperature; T_c is the crystallization peak temperature; X_c is the calculated degree of crystallinity.

Sample	T_c (°C)	T_m (°C)	X_c (%)
PP	121.1	163.4	61
PP-KL 2.5	117.9	163.5	54
PP-KL 5.0	114.2	163.1	56
PP-KL 10.0	113.3	163.0	58
PP-MAKL 2.5	115.3	163.5	47
PP-MAKL 5.0	113.8	164.1	48
PP-MAKL 10.0	112.6	163.1	49

The incorporation of lignin into polymer matrices can affect crystallinity in different ways. While it has the potential to act as a nucleating agent [35,36], other studies attribute a reduction in crystallinity to steric hindrance within the polymer's crystalline structure, as well as the inherently amorphous nature of lignin [15,16,37,38]. The DSC results obtained in this research indicate that while the melting temperature remained relatively stable across all samples, the crystallization temperature progressively decreased with increasing content of both KL and MAKL. Similarly, the degree of crystallinity declined with the addition of KL and MAKL, with neat PP exhibiting the highest crystallinity among the samples. This reduction was more pronounced in samples containing MAKL, indicating that the modification significantly impacts crystallinity, whereas the concentration appears to have minimal influence on this parameter.

Other studies in the literature have shown that esterified lignins can effectively influence the crystallization behavior of PP when incorporated into the polymer. Tanjung et al. [39] conducted a comparative study on the use of esterified alkaline lignin (AAL) and esterified organosolv lignin (AOSL) as interfacial modifying agents for PP-chitosan composites. Both modified lignins enhanced the interfacial adhesion within the composites.

Notably, the incorporation of AAL and AOSL led to a reduction in the crystallinity of the PP phase.

The incorporation of esterified lignin into PP significantly influences both the dispersion and crystallinity of the resulting blends through multiple potential mechanisms. One such mechanism is steric hindrance, resulting from the increased molecular free volume of the MAKL particles and the structural alterations introduced during esterification [40]. The addition of bulky functional groups and the extension of molecular chains significantly increase the spatial volume occupied by each particle, creating physical barriers that inhibit close packing and clustering [38,41]. This enhanced separation between particles promotes a more uniform distribution of MAKL within the PP, as evidenced by optical microscopy results.

The modification of lignin with maleic anhydride introduces aliphatic chains, which improve its dispersion within the polyolefin. These aliphatic chains enhance intermolecular interactions between lignin and PP, strengthening interfacial bonding and providing a more uniform distribution of lignin throughout the thermoplastic [37,42,43]. This improved compatibility facilitates the formation of well-defined interfaces, which disrupts the orderly arrangement of PP chains. As a result, these interfaces generate amorphous regions within the blends, hindering the growth and formation of large PP crystals, which ultimately contributes to a reduction in the degree of crystallinity.

The presence of lignin also reduces the mobility of PP chains, reducing their ability to organize into crystalline regions. In contrast, the mobility of KL is expected to increase after modification, likely due to the chain extension resulting from esterification with maleic anhydride. This increased mobility within the amorphous phase further limits the formation and growth of PP crystalline domains, leading to an overall reduction in crystallinity in the blends [40,44].

3.4. Viscoelastic Properties

Figure 5 presents the storage modulus (E′) and loss modulus (E″) curves for PP-KL (Figure 5a,b) and PP-MAKL (Figure 5c,d) samples as a function of temperature. Additionally, the insets highlight the tan δ (E″/E′) curves as a function of temperature, which are commonly used to characterize the polymer's T_g. The storage modulus reflects the elastic energy storage capacity of the material, serving as a key parameter for assessing load resistance [45]. Below room temperature, the glassy plateau characteristic of PP is slightly reduced by the addition of lignin, consistent with findings by Rezaei et al. [45], who reported a similar reduction when incorporating 10 wt% short carbon fibers into a PP matrix.

At higher temperatures (0–100 °C), the E′ values of PP-lignin composites surpass those of pure PP, attributed to the higher rigidity of lignin compared to PP [9,13,14]. However, the E′ values at 25 °C (Table 3) reveal that this increase is not proportional to lignin content. PP-MAKL samples exhibit a narrower E′ range (1.7–1.79 GPa) compared to PP-KL samples (1.62–1.84 GPa), indicating improved dispersion of MAKL lignin in the PP matrix, as supported by micrographs in Figure 4. With increasing temperature, E′ decreases continuously for both PP and the composites, a behavior widely reported in the literature and associated with enhanced polymer chain mobility at elevated temperatures [13,45,46].

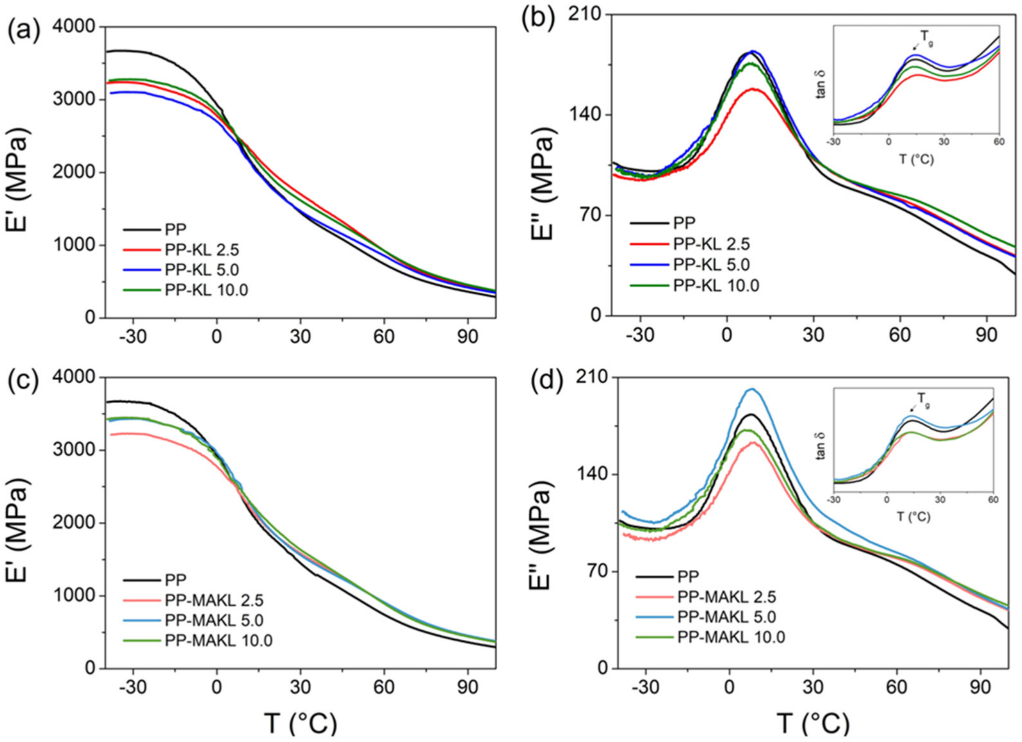

Figure 5. E′ and E″ curves of the (**a**,**b**) PP-KL and (**c**,**d**) PP-MAKL. The insets display the tan δ curves as a function of temperature, which identify the Tg of the blends.

Table 3. Values of T_g and E′ from DMA.

Sample	E′ @25 °C (GPa)	T_g (°C)
PP	1.61	13.07
PP-KL 2.5	1.84	13.45
PP-KL 5.0	1.61	13.51
PP-KL 10.0	1.75	13.19
PP-MAKL 2.5	1.71	13.41
PP-MAKL 5.0	1.70	13.21
PP-MAKL 10.0	1.79	13.17

The loss modulus quantifies the material's capacity to dissipate energy, either as heat or via molecular rearrangements during deformation, and corresponds to the viscous component of the material [45]. Maximum energy dissipation occurs during the α-transition of PP [46], between −20 °C and 30 °C, and can be associated with the material's T_g, as determined from the tan δ peak [47]. The T_g values for PP-lignin composites are summarized in Table 3, showing a discrete and consistent increase with lignin addition. This trend is generally attributed to the restriction of polymer chain mobility imposed by the complex and highly branched structure of lignin [3]. In this case, the T_g values for the PP-KL and PP-MAKL blends are similar, indicating that the restriction effect is more associated with the presence of lignin rather than its concentration or specific interaction. This behavior is consistent with previously reported results for kraft lignin in ethylene-butylene matrix composites [9].

On the other hand, the magnitude of energy dissipation varies among the composites. KL addition has minimal effect on E″, while 5 wt% MAKL significantly increases dissipation, as evidenced by the higher E″ values relative to pure PP. This effect can be ascribed to an increase in the amorphous fraction of the composites, as evidenced by DSC analysis, which reflects the inherently amorphous structure of lignin. Additionally, the improved interaction between PP and MAKL, compared to PP-KL, contributes to this behavior. Moreover, the enhanced energy dissipation observed at the interface between the flexible polymer matrix and the rigid lignin is more prominent in samples with MAKL. This is attributed to the stronger interfacial interaction between MAKL and the PP matrix, leading to a greater number of contact interfaces. Similar behavior was reported by De Sousa et al. [3], who observed increased interfacial energy dissipation in SEBS block copolymers containing kraft lignin, specifically at the interface between the flexible ethylene-butylene segments and lignin. In contrast, the PP-MAKL 10 sample exhibits a slight reduction in E″ magnitude, showing behavior similar to pure PP and the PP-KL 10 sample. This effect is attributed to the formation of larger MAKL aggregates in the PP matrix at higher lignin concentrations, which reduces the efficiency of interfacial energy dissipation.

3.5. Mechanical Properties

The mechanical behavior of lignin-polymer blends has been extensively explored in the literature [13,14,20,22,25,44,48,49]. Incorporating lignin generally increases the elastic modulus of the blends, as indicated by DMA at the temperature of 25 °C, due to lignin's high intrinsic rigidity. On the other hand, ultimate tensile strength is more sensitive to interactions between blend components, making it a key parameter for assessing interfacial compatibility [9,15]. Figure 6a shows the yield strength (σ_y) of PP-KL and PP-MAKL samples as a function of lignin concentration. Regardless of the lignin type, its addition decreases σ_y. This behavior, previously observed in polyolefin matrices, is attributed to the low chemical affinity between PP and lignin due to the inherent differences in their chemical structures [13,20,33]. Higher lignin concentrations result in reduced mechanical strength, which is associated with the formation of larger lignin aggregates. This phase separation hinders efficient interfacial stress transfer, leading to lower tensile strength in PP-KL and PP-MAKL blends compared to pure PP [33,42]. A previous study [22] indicated that the addition of up to 10 wt% of esterified lignin to the PP matrix results in materials with mechanical properties comparable to pure PP, demonstrating good compatibility between PP and MAKL. In this study, while there is a slight tendency for higher σ_y values in MAKL composites compared to KL, these values remain within experimental error. This behavior can be attributed to the relatively low lignin concentration (up to 10 wt%), as previous studies have reported more significant decreases in tensile strength at higher concentrations of esterified lignin [22].

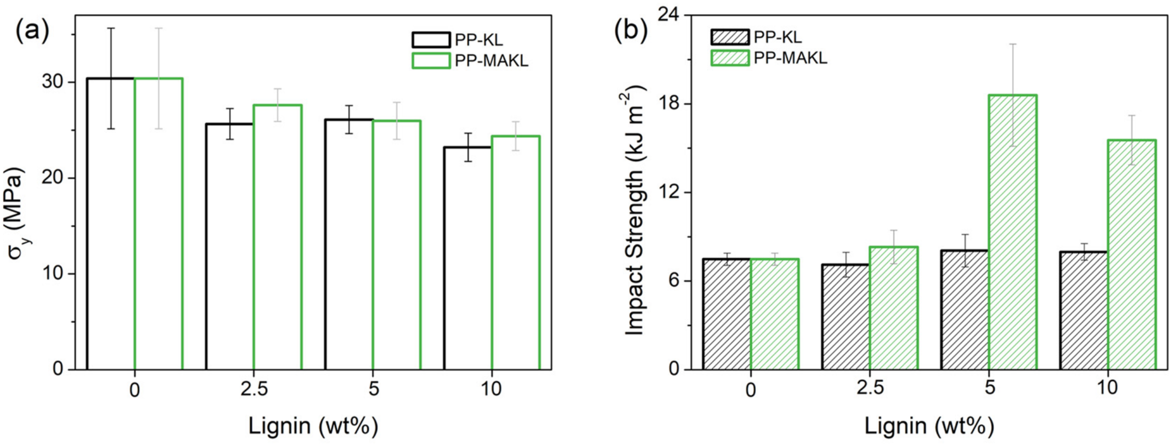

Figure 6. (**a**) Yield stress (σ_y) and (**b**) impact strength of PP-KL and PP-MAKL samples.

Figure 6b presents the impact strength of blends with KL and MAKL. While KL addition does not significantly affect PP's impact strength, incorporating 5 wt% and 10 wt% of MAKL increases impact resistance by 148% and 108%, respectively. The literature reports varying behaviors regarding the impact strength of PP-lignin blends. In some cases, lignin—whether unmodified, esterified, or alkylated—reduces impact resistance, primarily due to its rigidity, which promotes embrittlement [14,22]. Conversely, Chen et al. [48] observed a 35% increase in impact strength when incorporating 10 wt% of alkylated lignin into PP. Although higher lignin concentrations led to declines in impact strength, values remained superior to pure PP up to 40 wt% of lignin. According to the authors, this is likely due to the enhanced interaction between alkylated lignin and the PP matrix, facilitated by added aliphatic chains.

In this work, the enhanced impact strength observed with MAKL incorporation can be attributed to two factors: (i) improved interaction between modified lignin and PP, and (ii) an increased amorphous fraction, which enhances energy dissipation. Improved interaction is supported by the known influence of particle size and dispersion on the impact strength of multiphase materials; smaller, well-dispersed particles effectively hinder crack propagation [50,51]. The increase in the amorphous fraction, observed in DMA analyses, was most pronounced for the PP-MAKL 5 sample, which exhibited maximum energy dissipation. This behavior arises from both the increased amorphous content of the material and the enhanced interfacial dissipation between phases, which contribute to the improved cohesive strength [3]. However, the PP-MAKL 10 sample, although exceeding pure PP in impact strength, exhibited lower values compared to PP-MAKL 5. This is likely attributed to the formation of larger lignin aggregates, which reduce energy dissipation efficiency and act as sites of embrittlement. Thus, the results indicate a synergistic effect in PP-MAKL blends, where enhanced phase compatibility and improved viscoelastic properties contribute to superior impact strength at specific compositions.

4. Conclusions

This study demonstrated that the modification of kraft lignin through a simplified esterification process with maleic anhydride (MAKL) resulted in significant improvements in the properties of PP blends. The modification was confirmed by FTIR and DSC analyses. Optical microscopy images revealed a more uniform dispersion of MAKL in PP compared to unmodified lignin, indicating enhanced interfacial compatibility resulting from grafting aliphatic chains onto the lignin surface. Thermal analysis via DSC showed that the addition of MAKL did not significantly alter the T_m of PP but led to a marked decrease in crystallinity. This change was attributed to the improved interaction between PP and the modified lignin, which restricted polymer chain mobility and hindered crystallization. Viscoelastic properties, evaluated by DMA, further corroborated these findings, showing a slight increase in the T_g and an increase in energy dissipation, reflecting a higher amorphous content and enhanced interfacial energy dissipation. From a mechanical perspective, the impact strength of the PP-MAKL blends was significantly improved, with an increase of up to 148% upon the incorporation of 5 wt% MAKL, which was attributed to better lignin dispersion and interfacial energy dissipation. In conclusion, esterification of kraft lignin with maleic anhydride proved to be an effective strategy for enhancing the dispersion, thermal, viscoelastic, and mechanical properties of PP blends. These findings provide valuable insights into the potential of using modified lignin as a sustainable component in polymer blends with improved performance.

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