

Article

Improved Thermo-Mechanical and Flame Resistance Behaviour of Polyamide 6/Lignin Microcomposites

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Abstract

This work focused on the investigation of sulfonated lignin as a novel and sustainable reinforcing filler for polyamide 6 (PA6) composites. Different formulations were thus prepared by melt compounding, varying the lignin content (5, 10, and 20 wt%). The interaction between lignin and PA6 was systematically studied through rheological, structural, morphological, thermo-mechanical, and flammability tests. Rheological measurements showed an increase in the complex viscosity and viscoelastic moduli with increasing lignin content, suggesting restricted polymer chain mobility and the formation of strong physical interactions between the molten PA6 and the lignin particles. Microstructural observations through FESEM highlighted a good dispersion of lignin particles and efficient filler–matrix interfacial adhesion. Moreover, the addition of lignin significantly increased the tensile stiffness of the composites (up to 3.4 GPa), and a lignin content of 10 wt% enhanced the tensile strength up to 58.4 MPa (i.e., +45% compared to neat PA6) without compromising the ductility. Finally, UL-94 tests revealed an improvement in flame retardancy at higher lignin contents due to the intrinsic char-forming ability of this filler. These results demonstrated that lignin could be an effective multifunctional bio-based filler that can improve the thermo-mechanical performance of PA6 without the need for compatibilizing agents.

Keywords: polyamide 6; lignin; composites; mechanical properties; adhesion; flammability

1. Introduction

The use of natural and organic fillers, such as lignin and cellulose fibres, offers several advantages, including high mechanical properties per unit mass, biodegradable nature, CO₂ neutrality, and abundant availability from renewable resources [1,2]. Lignin is the second most abundant biopolymer in the world and constitutes one of the primary components of wood, thereby enhancing the rigidity of cell walls within the plant structure [3,4]. Lignin is a highly complex, amorphous aromatic biopolymer that is considerably more heterogeneous than cellulose and hemicellulose, owing to its irregular, three-dimensional, and highly branched phenolic structure [5,6]. It is bio-synthesized from three primary phenylpropane monolignols (p-coumaryl, coniferyl, and sinapyl alcohols), which serve as the precursors for p-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) structural units, respectively [7,8]. These monolignols are interconnected through radical coupling reactions, forming a variety of ether and carbon–carbon linkages, with β -O-4 ether bonds accounting for approximately 50–60% of the total interunit connections [9,10]. As a naturally occurring



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material, the composition and properties of lignin exhibit significant variability depending on the origin, growth conditions, and extraction processes. For instance, softwood lignin is predominantly composed of G units with minor amounts of H units, whereas hardwood lignin mainly contains G and S units with traces of H constituent [11,12]. Industrially, lignin is produced in large quantities from the pulp and paper industry and second-generation ethanol biorefineries, which together generate an estimated 100 million tons of lignin annually worldwide [13–15]. To address the inherent variability of native lignin, industrial processing techniques are employed to produce technical-grade lignins with specific functional groups and more consistent properties. Consequently, most commercially available lignins are mainly by-products of different pulping processes. Among these, sodium lignosulfonate (NaLS), derived from the sulfite pulping of wood, is the most widely traded technical lignin [16,17]. In material science, lignin is currently establishing itself as a low cost and environmentally friendly filler for sustainable polymer–matrix composite materials. Numerous studies have investigated the addition of lignin into commercial polymers, including polypropylene (PP) [18,19] and epoxy [20,21], as well as bio-based polymers such as polylactic acid (PLA) [22], chitosan [23], starch [24,25], and cellulose [26]. However, most of these studies rely on compatibilizing agents or chemical modification of lignin to achieve substantial improvements in physical properties. This limitation is primarily attributed to the poor miscibility of lignin with non-polar polymers, where lignin tends to aggregate due to its intermolecular hydrogen bonding, π - π stacking, aromatic groups, and van der Waals interactions between polymer chains [27,28]. On the other hand, the polarity of lignin could promote good interactions with polar polymers, as strong intermolecular bonds between the polymer matrix and the polar functional groups of lignin can be formed, resulting in enhanced interfacial adhesion [29]. Various studies have investigated the interaction of lignin with polar matrices, including poly(ethylene oxide) (PEO) and poly(ethylene terephthalate) (PET), through thermal analysis and Fourier-transform infrared spectroscopy (FTIR) [30,31]. Specifically, strong intermolecular hydrogen bonds between the ether groups of PEO with aliphatic hydroxyl groups of lignin were observed.

Among the most relevant technical lignin products, NaLS presents both hydrophilic functional groups, such as sulfonate and carboxylic groups, and hydrophobic aliphatic and aromatic moieties, making it an interesting filler with surface-active behaviour [32]. Furthermore, the chemical modification of NaLS enables the extraction of a lignin with a high sulfonate group content. This results in a highly polar and ionic material that can be easily dispersed in polar polymer matrices. Consequently, this favourable interaction has the potential to improve the thermal and the mechanical properties of the resulting bio-composites, without the need of compatibilizers or filler surface treatments [33].

Despite these interesting aspects, the use of sulfonated lignin as a reinforcing filler for polar engineering polymers remains an under-researched area in the existing literature. Among these polar polymers, polyamide 6 (PA6) is widely recognised as a promising matrix material for the development of high-performance composites [34–36]. To the best of our knowledge, the potential of lignin in PA6-composites has been examined only once [37], leaving several key aspects, such as the type of the lignin used, insufficiently understood and requiring further investigation. In this context, the present study aims to provide a systematic and more comprehensive evaluation of the role played by a commercial lignin filler, derived from NaLS, in a PA6 matrix. In particular, the present work includes: a detailed rheological analysis to study the melt behaviour and polymer–filler interactions; microstructural characterisation through FESEM to assess dispersion and interfacial adhesion; thermo-mechanical testing; and UL-94 flammability assessment.

2. Materials and Methods

2.1. Materials

The thermoplastic matrix used in this study was an ECONYL ECO27 R24424 polyamide 6 supplied by Aquafil S.p.A. (Arco, Italy) in pellet form (density = 1.11 g/cm^3 , melting temperature = 221°C , molecular weight (M_w) = $60,000 \text{ g/mol}$). Commercial lignin (alkaline) used as a filler was purchased by Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan) in the form of black powder (density = 1.23 g/cm^3 , methoxyl groups = 10–12%). As specified by the supplier, this lignin was derived from the partial desulfonation, oxidation, hydrolysis, and demethylation of sodium liginosulfonate, followed by pH adjustment.

2.2. Sample Preparation

Materials were dried in an oven at 60°C for 48 h before use. PA6 granules were melt-compounded with lignin filler through a Thermo Haake Rheomix 600 internal mixer (ThermoFisher Scientific Inc., Watham, MA, USA) equipped with counter-rotating rotors, operating at 60 rpm and a temperature of 235°C for 6 min. The lignin was added to PA6 at three different concentrations (5 wt%, 10 wt% and 20 wt%) after 4 min and then the mixture was left to mix for 2 min. The resultant blends were then granulated using a Piovan[®] RN166/1 granulator (Piovan SpA, Venice, Italy), to produce granules with a size of approximately 2 mm. The obtained granules were then compression-moulded in a Carver hot-plate press at 235°C for 8 min, under an applied pressure of 4.9 MPa. In this way, square sheets $100 \times 100 \times 1 \text{ mm}^3$ were prepared. The produced samples are denoted as PA6_xLignin, where x is equal to 5, 10, or 20, depending on the weight fraction of lignin. A sample with neat PA6 was also prepared for comparison.

2.3. Experimental Techniques

2.3.1. Rheological Analysis

The rheological properties of the samples were investigated using a Discovery hybrid rheometer DHR-2 (TA Instruments, New Castle, DE, USA) operating in parallel plate configuration, adopting a plate diameter of 25 mm and setting a gap distance of 1 mm. The tests were conducted at a constant temperature of 250°C in oscillatory mode with a frequency range between 0.05 and 600 rad/s. From these tests, the complex viscosity (η^*), storage modulus (G'), loss modulus (G''), and loss factor ($\tan\delta$) as a function of the frequency were determined.

2.3.2. Fourier-Transform Infrared Spectroscopy (FT-IR)

Fourier-transform infrared spectroscopy (FT-IR) was performed on composite samples in order to investigate the chemical interaction between lignin and the PA6 matrix. The tests were conducted in attenuated total reflectance (ATR) mode using a PerkinElmer Spectrum One spectrometer (PerkinElmer, Waltham, MA, USA) equipped with a zinc selenide crystal and a built-in force sensor allowing controlled and reproducible pressure application. The spectra were measured in the wavenumber range of $650\text{--}4000 \text{ cm}^{-1}$, obtaining each spectrum from the superposition of four scans.

2.3.3. Microstructural and Physical Characterisation

Micrographs of cryo-fractured cross-sections of the samples were obtained using a Zeiss Supra 40 field emission scanning electron microscope (FESEM) (Carl Zeiss AG, Oberkochen, Germany), operating at an accelerating voltage of 3.5 kV inside a chamber under a vacuum of 10^{-6} Torr. Prior to the observations, the samples were dried in a fan oven at 50°C for 48 h and then coated with a thin electrically conductive platinum/palladium (Pt/Pd) layer.

The density of the samples was measured to calculate their porosity. Specifically, the theoretical density (ρ_{th}) of the composites was evaluated with the rule of mixtures, by knowing the apparent densities and the nominal weight fractions, according to Equation (1):

$$\rho_{th} = \frac{1}{\sum_i \frac{W_i}{\rho_i}} = \frac{1}{\frac{W_{PA6}}{\rho_{PA6}} + \frac{W_{Lignin}}{\rho_{Lignin}}} \quad (1)$$

where W_{PA6} and W_{Lignin} are the weight fractions of the PA6 and lignin, respectively, and ρ_{PA6} and ρ_{Lignin} are their apparent densities. The apparent densities, corresponding to the volume together with only the closed porosity, were measured using the AccuPyc 1330 helium pycnometer (Micromeritics Instrument Corporation, Norcross, GA, USA). For every composition, a specimen was tested and inserted in a chamber with a volume of 1 cm³. Every measurement was collected at a constant temperature of 23 °C, and 99 measurements were performed for each specimen. The apparent density was then calculated as the average of all measurements. The bulk density (ρ_{bulk}), which comprises both the open and the closed porosity, was calculated as the ratio between the mass and the volume of 20 × 5 × 1 mm³ specimens. The dimensions of the specimens were measured with a digital calliper (d = 0.01 mm) and the mass was measured with an analytical balance (d = 0.0001 g). Five specimens were measured for each composition. Finally, the total porosity (P_{tot}) was calculated according to Equation (2):

$$P_{tot} = 1 - \frac{\rho_{bulk}}{\rho_{th}} \quad (2)$$

2.3.4. Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) was performed using a Mettler DSC5+ (Mettler Toledo Inc., Columbus, OH, USA). Specimens of approx. 10 mg were sealed in aluminium crucibles and subjected to a first heating ramp from 0 °C to 260 °C at a rate of 10 °C/min under a constant nitrogen flow of 100 mL/min in order to erase the previous thermal history. Subsequently, the samples were cooled and reheated from 0 °C to 260 °C at a rate of 10 °C under a constant nitrogen flow of 100 mL/min. The tests enabled the measurement of the melting and crystallisation temperatures (T_m , T_c), and the corresponding specific enthalpy values (ΔH_m and ΔH_c). Furthermore, the degree of crystallinity was calculated according to Equation (3):

$$\chi = \frac{\Delta H_m - \Delta H_{cc}}{\Delta H_{m,th} \cdot \omega} \cdot 100 \quad (3)$$

where ΔH_{cc} is the cold crystallisation enthalpy of PA6; $\Delta H_{m,th}$ is the enthalpy of melting of fully crystalline PA6, equal to 229.7 J/g [38]; and ω is the weight fraction of PA6 in the composites.

2.3.5. Dynamic Mechanical Thermal Analysis (DMTA)

Dynamic mechanical thermal analysis was carried out using a TA Q800 DMA instrument (TA instruments, New Castle, DE, USA). Tests were carried out in tensile mode on rectangular specimens with nominal dimensions of 10 × 5 × 1 mm³, in a temperature range from 0 °C to 150 °C at a heating rate of 3 °C/min, applying a strain amplitude of 0.05% and a frequency of 1 Hz. These experiments allowed the measurement of the storage modulus (E') and the loss modulus (E'') as a function of temperature. At least 3 specimens were tested for each composition.

2.3.6. Mechanical Properties

Quasi-static tensile tests were performed using an Instron 5969 (Instron, Norwood, MA, USA) testing machine equipped with a load cell of 10 kN and operating at a crosshead speed of 2 mm/min, for the determination of the maximum tensile stress (σ_{max}) and the elongation at break (ϵ_b). The elastic modulus (E) was determined with an Instron 2620-601 extensometer, having a gauge length of 12.5 mm, at a crosshead speed of 0.25 mm/min. E was calculated as the secant modulus considering the stress levels associated with the strain values of 0.05% and 0.25%. The tensile tests were carried out on ISO 527 1BA [39] specimens and at least 5 specimens were tested for each composition. The specimens were dried in an oven at 60 °C for over 24 h and were analysed immediately afterward.

2.3.7. Flame Behaviour

The evaluation of the flammability was conducted in accordance with the UL-94 [40] methodology in both the horizontal burning (HB) and vertical burning (V) configurations. Tests were performed on $125 \times 10 \times 4$ mm³ rectangular specimens. In both configurations, the specimens were exposed to a 20 mm high flame at the edge for 10 s and the burning time after first ignition (t_1) was recorded. Thereafter, as soon as afterflaming of the specimen had ceased, the burner was repositioned at the edge of the specimen for a further 10 s to initiate a second ignition. The second burning time (t_2) was also recorded, and the occurrence of dripping of the molten material was monitored throughout the test. Based on these observations, the materials were classified into the appropriate flammability categories, i.e., HB, V-2, V-1, or V-0. At least 5 specimens were tested for each composition.

2.3.8. Statistical Analysis

All the results are presented as mean $\pm$ standard error of the mean. Data were analysed by using one-way analysis of variance (ANOVA) with a significance level of 0.05. Pairwise differences between treatments were assessed using the post hoc Tukey's test.

3. Results and Discussion

3.1. Rheological Analysis

Figure 1a–d show the results of the rheological investigation performed on neat PA6 and lignin-reinforced composites to investigate their processability and the filler–matrix interaction.

The addition of lignin in the polymer matrix leads to a simultaneous increase in complex viscosity, storage modulus, and loss modulus, and this effect becomes progressively more pronounced as the lignin content increases. This behaviour indicates the occurrence of physical interactions between lignin particles and the polymer matrix, which hinder the mobility of PA6 macromolecules in the molten state, thereby enhancing their resistance to flow [41]. As observed from the complex viscosity curves (Figure 1a), lignin-reinforced composites exhibit more pronounced shear-thinning behaviour compared to the neat PA6, as indicated by the stronger decrease in viscosity with increasing frequency [42,43]. Furthermore, at low frequencies, the lignin-filled composites show the presence of a yield stress, which becomes higher with increasing lignin content. These responses are typical of polymer composites containing dispersed fillers and are often associated with the disruption of polymer–filler interactions under shear [44]. At higher frequencies, the differences in viscosity between neat PA6 and lignin-filled composites become less pronounced, indicating that the polymer chain dynamics dominate the melt response under these conditions [45]. For all samples, the loss modulus values are higher than the corresponding storage modulus ones over the entire frequency range, which suggests a preponderance of the viscous component over the elastic one [46]. From loss factor curves (Figure 1d), it can be noticed that

the $\tan\delta$ values decrease with the lignin content; this trend is coherent with the stiffening effect provided by the lignin introduction. However, the values of $\tan\delta$ remain higher than 1 for all the compositions over most of the investigated frequency range, indicating that the composites retain a predominantly liquid-like behaviour, which is favourable for melt processing [47].

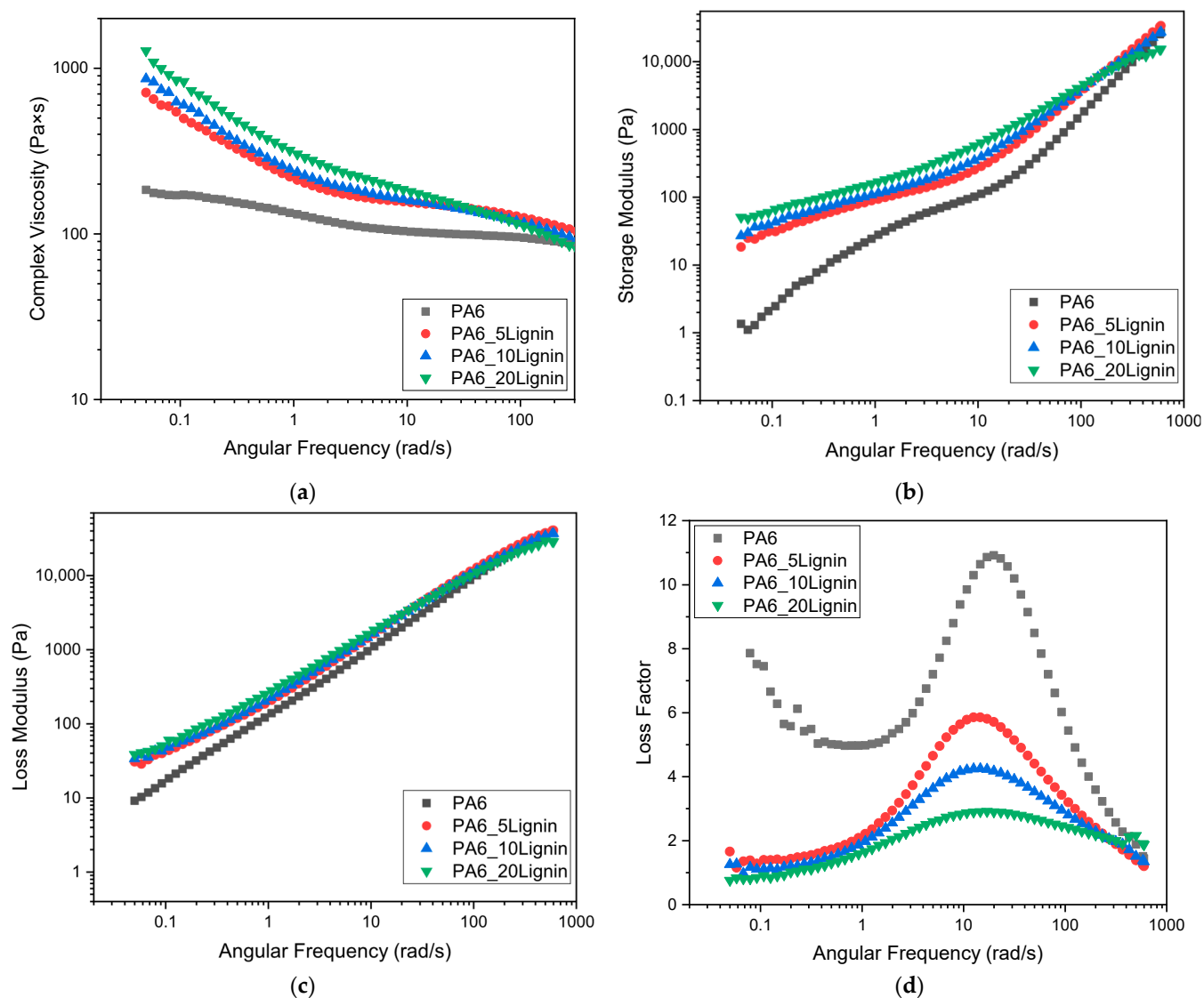


Figure 1. Rheological behaviour at 250 °C of the produced composites. Trends of (a) complex viscosity; (b) storage modulus; (c) loss modulus; and (d) loss factor ($\tan\delta$) as a function of the angular frequency.

3.2. Fourier-Transform Infrared Spectroscopy (FT-IR)

Figure 2 shows the FT-IR spectra of the lignin particles, of neat PA6 matrix, and of the relative lignin-filled composites.

In neat PA6, the broad absorption peak at 3297 cm^{-1} is attributed to N-H stretching vibration in primary amine, while the two peaks at 2930 cm^{-1} and 2860 cm^{-1} are associated with the asymmetric and symmetric stretching vibrations of the CH_2 group, respectively [48]. The peaks at 1637 cm^{-1} and 1535 cm^{-1} are attributed to the C=O stretching of amide I, and the combination of N-H bending and C-N stretching of amide II, respectively [49]. The peak at 1263 cm^{-1} is associated with the combination of C-N stretching and N-H bending of amide III [50]. From the lignin spectrum, it is possible to observe a broad band at 3300 cm^{-1} corresponding to O-H stretching vibration of hydroxyl groups, a peak at 1582 cm^{-1} associated with the C=C aromatic skeletal vibrations, and peaks between

1204 cm^{-1} and 1032 cm^{-1} , attributed to the C-O stretching vibration of phenolic and ether groups [51]. Upon the addition of lignin in the PA6 matrix, the spectra mainly retain the main absorption features of PA6 neat. However, the N-H stretching band of PA6 is slightly shifted with increasing lignin content (from 3297 cm^{-1} of neat PA6 to 3294 cm^{-1} of PA6-20Lignin), while minor shifts and peak intensity reduction are also observed in the amide I and amide II bands. These effects may suggest the formation of intermolecular hydrogen bonds between the amide groups of PA6 and the polar phenolic and aliphatic hydroxyl groups of lignin, as also reported in the literature [37]. Such interactions are in agreement with the results of the rheological tests and highlight a good interfacial interaction between PA6 and lignin. However, further analysis will be carried out in order to assess the interactions between matrix and filler through additional chemical state analysis (e.g., XPS and solid-state NMR).

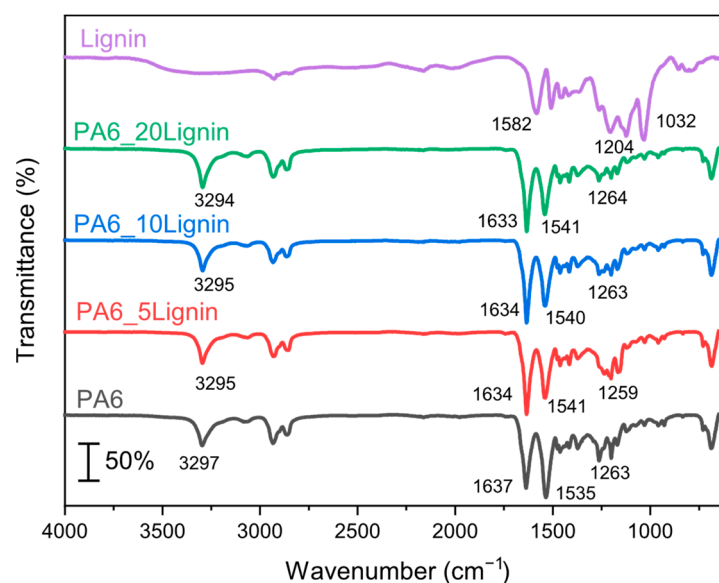


Figure 2. FT-IR spectra of the lignin particles, neat PA6, and the relative composites.

3.3. Microstructural and Physical Characterisation

Figure 3a–f show the microstructural and physical characterisation carried out on the neat PA6 and composites.

Figure 3a shows the FESEM micrograph of the lignin particles, which exhibit a spheroidal morphology with a relatively broad particle size distribution, ranging from 20 μm to 70 μm (mean $35 \pm 15 \mu\text{m}$). From Figure 3b–e it is possible to observe that the addition of lignin leads to a progressively rougher and brittle fracture surface in comparison to the homogeneous surface of neat PA6. The lignin particles are clearly visible and well dispersed within the PA6 matrix with a good interfacial adhesion between the matrix and the filler, even in absence of compatibilizing agents. The grooves observed at higher lignin content (20 wt%) are mainly attributed to intraparticle microcracking rather than interfacial debonding between matrix and filler, suggesting that partial particle breakage occurred during the sample preparation.

Figure 3f shows that the addition of lignin leads to a progressive increase in both the apparent and bulk densities of the composites. This trend is expected since lignin has a higher density (1.23 g/cm^3) than PA6 (1.11 g/cm^3). The porosity values, evaluated according to Equation (2), are close to 1 vol% for all the samples and no statistically significant differences ($p < 0.05$) are observed by varying the lignin content. These results indicate good processability and effective filler–matrix adhesion, as also observed from FESEM analysis.

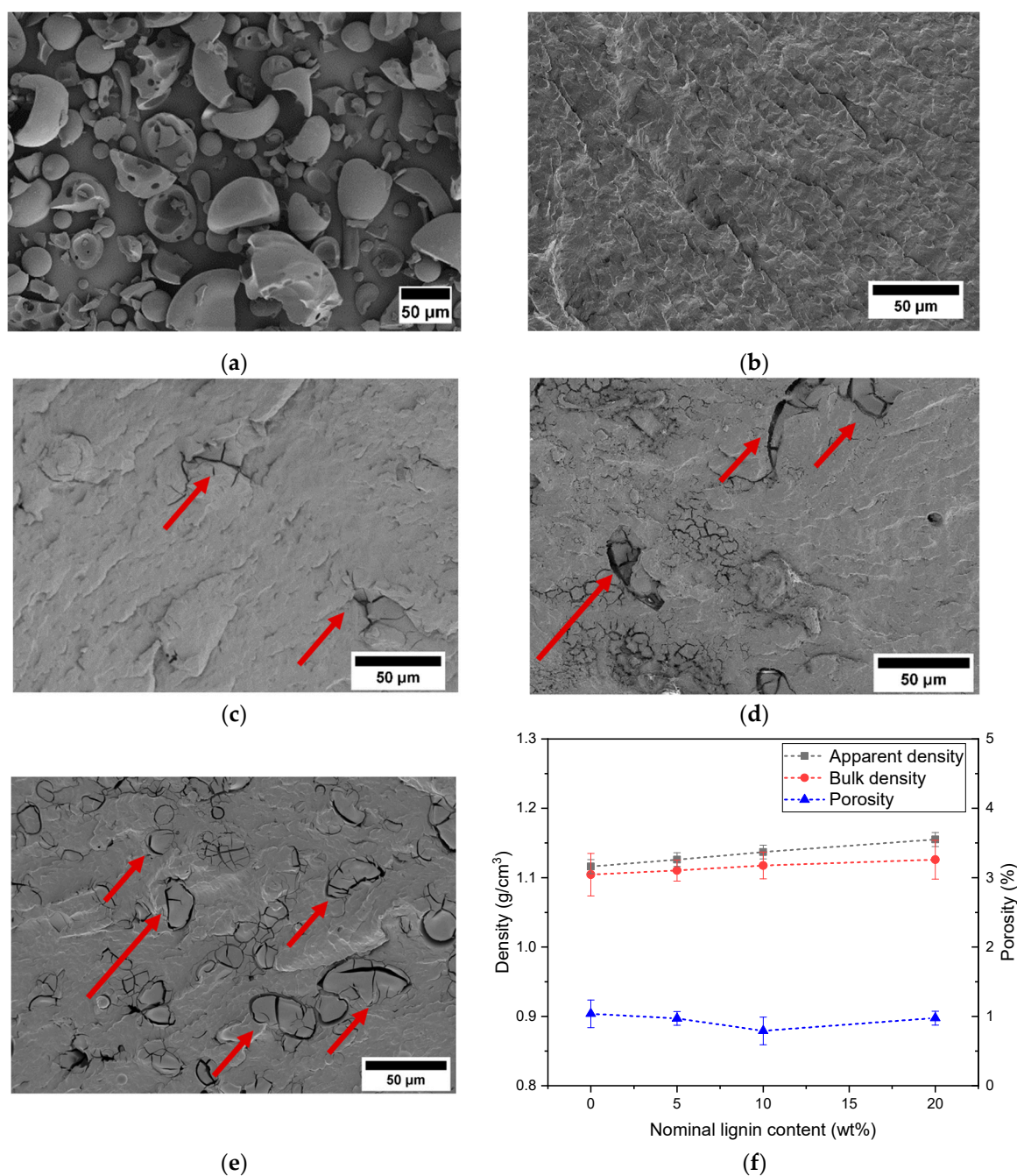


Figure 3. Microstructural and physical characterisation of the samples: (a) lignin particles; (b) PA6 neat; (c) PA6_5Lignin; (d) PA6_10Lignin; (e) PA6_20Lignin; (f) apparent density, bulk density and porosity as a function of the lignin content. Red arrows indicate the lignin domains.

3.4. Differential Scanning Calorimetry (DSC)

Figure 4a–c and Table 1 report the results of DSC analysis of neat PA6 and the relative composites, which was performed to assess their thermal behaviour and investigate the interaction between PA6 and lignin.

The thermograms of neat lignin were not reported, since no significant signals were observed across the entire temperature range. For all the composites, both the melting and the crystallisation temperatures decrease with increasing lignin content, with a shift of approximately 6 °C observed for T_c . Such variation suggests an effect of lignin on the crystallisation behaviour of the polymer matrix. This behaviour can be attributed to restricted chain mobility and hindered crystal growth induced by the presence of lignin, as

reported in the literature [37]. In addition, residual moisture associated with lignin may have promoted slight polymer degradation, further influencing the crystallisation process. Despite the shift in T_c , the degree of crystallinity (Equation (3)) remains constant across all samples. This indicates that lignin primarily affects the crystallisation kinetics, while the overall crystalline fraction remains substantially unchanged. The progressive decrease in both melting and crystallisation enthalpies is consistent with the decrease in the polymer matrix fraction. The T_g values were not reported, due to the small intensity of the signal associated with this transition, suggesting that the influence of lignin on the mobility of the PA6 chain segments cannot be assessed by DSC alone. Therefore, further investigations into the glass transition temperature were conducted through DMTA.

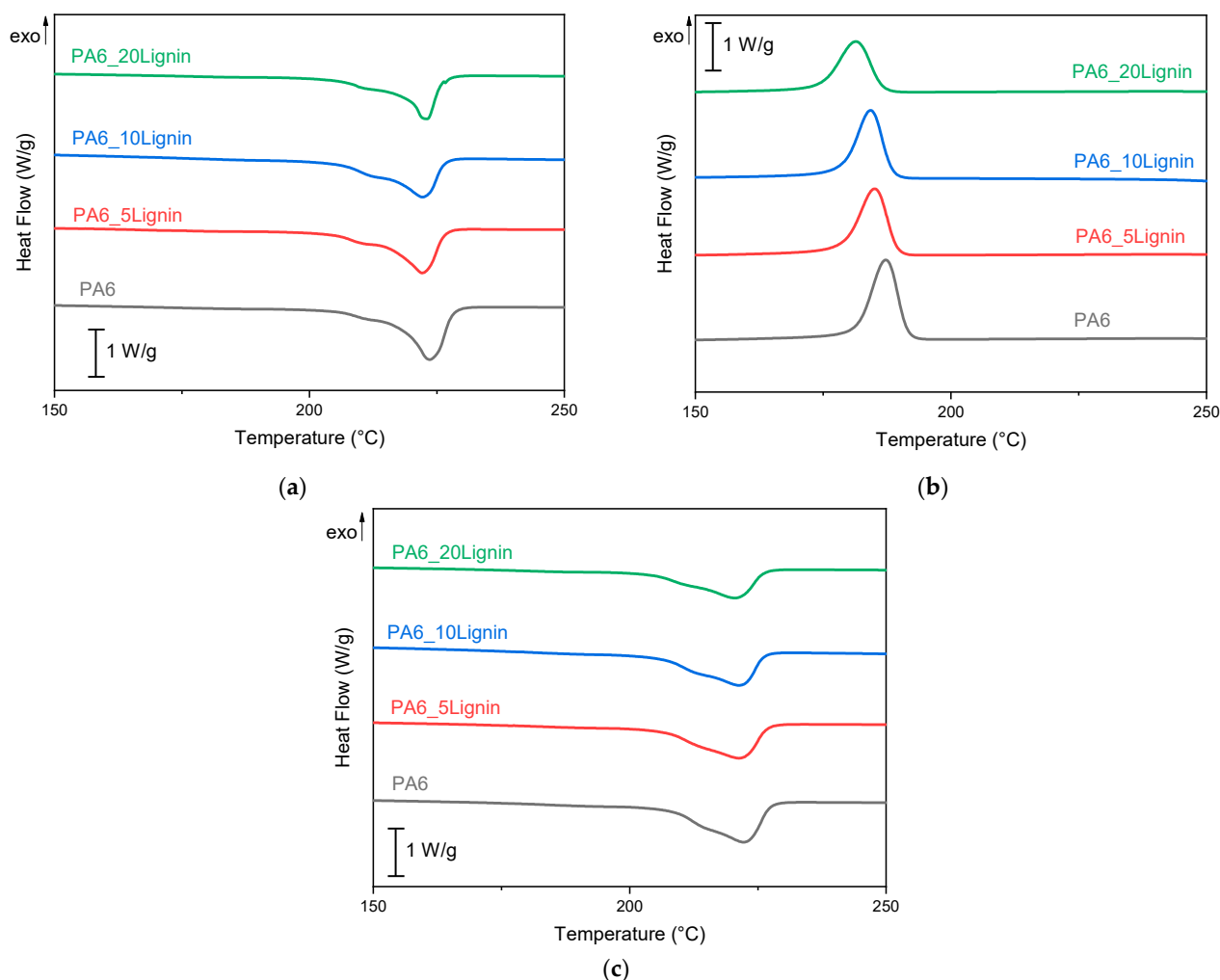


Figure 4. DSC thermograms of the prepared composites. (a) First heating scan; (b) cooling scan; (c) second heating scan.

Table 1. DSC results for the prepared composites.

Sample	T_{m1} (°C)	ΔH_{m1} (J/g)	χ_1 (%)	T_c (°C)	ΔH_c (J/g)	T_{m2} (°C)	ΔH_{m2} (J/g)	χ_2 (%)
PA6	223.4	62.0	27.0	187.6	69.7	221.9	71.8	31.3
PA6_5Lignin	221.9	60.7	27.8	185.6	65.3	221.0	66.4	30.4
PA6_10Lignin	221.8	60.2	29.1	184.8	61.6	221.1	61.6	29.8
PA6_20Lignin	221.6	52.1	28.4	181.6	55.1	220.3	55.3	30.1

T_{m1} , ΔH_{m1} = melting temperature and enthalpy (first heating scan); T_c , ΔH_c = crystallisation temperature and enthalpy (cooling scan); T_{m2} , ΔH_{m2} = melting temperature and enthalpy (second heating scan); χ_1 , χ_2 = degree of crystallinity (first and second heating scan).

3.5. Dynamic Mechanical Thermal Analysis (DMTA)

Figure 5 shows the results of DMTA performed on neat PA6 and the relative composites, performed in order to better investigate the effect of lignin on the glass transition range.

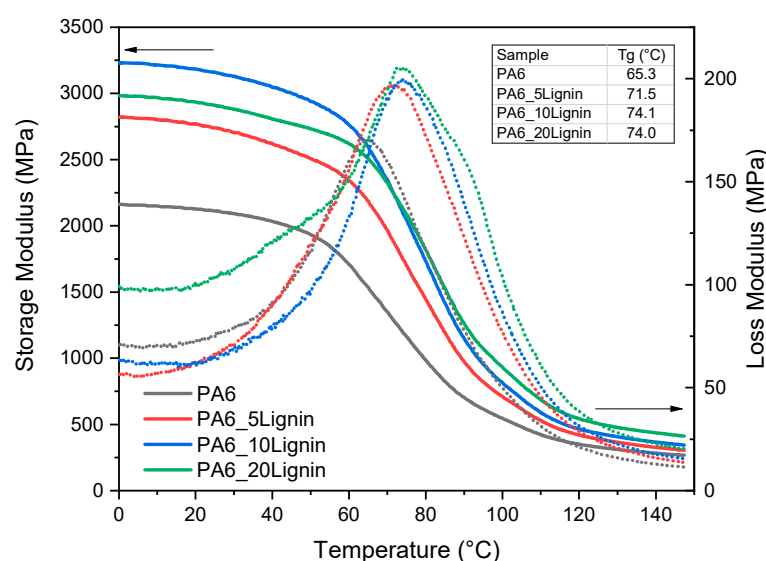


Figure 5. Results of DMTA tests on neat PA6 and the relative composites, and trends of storage modulus (E') and loss modulus (E'') as a function of the temperature.

From Figure 5, a clear effect of the lignin addition on the viscoelastic properties of PA6-based composites can be observed. The glass transition range, commonly identified by the peak of the loss modulus curves, progressively shifts towards higher temperature with increasing lignin content. Specifically, the T_g passes from 65 °C for neat PA6 to approximately 74 °C for composites with higher lignin contents. This behaviour confirms the restriction of segmental mobility of the PA6 chains due to the presence of lignin, specifically attributed to the physical interactions between the polymer matrix and polar functional groups of lignin. From the storage modulus curves, it can be noticed that all lignin-reinforced composites exhibit higher modulus values than neat PA6 over the entire temperature range. Specifically, at both 25 and 120 °C (i.e., below and above T_g), the storage modulus increases by up to 44% for composites with higher lignin contents compared to neat PA6. This demonstrates a higher good thermo-mechanical stability due to the stiff nature of lignin particles.

3.6. Mechanical Properties

Figure 6a–d report the results of quasi-static tensile tests carried out on neat PA6 and the relative composites.

The stress–strain curves reported in Figure 6a clearly show that the addition of lignin leads to a more brittle fracture behaviour of the materials. From the results of elastic modulus reported in Figure 6b, it is possible to observe that the addition of lignin significantly enhances ($p < 0.05$) the stiffness of PA6 composites. Specifically, the elastic modulus increases from 2.8 GPa for neat PA6 to around 3.3 GPa (+18%) for all lignin-reinforced composites. This confirms the stiffening effect provided by lignin, which is consistent with the increased storage modulus observed in DMTA measurements. The mechanical strength also seems to benefit from the introduction of lignin. From Figure 6c, the sample containing 10wt% lignin exhibits a statistically significant increase ($p < 0.05$) in maximum tensile strength compared to all other samples (+ 45% with respect to neat PA6). This result indicates an optimal filler loading at which the reinforcing effect is maximised. Indeed, the samples with 5 wt% and 20 wt% of lignin do not statistically differ from neat PA6,

suggesting that a lower lignin content may be insufficient to achieve effective reinforcement, while higher loadings may promote filler agglomeration. From Figure 6d, it is possible to notice that there is a slight and progressive decrease in the elongation at break as the lignin content increases. However, this reduction is not statistically significant ($p < 0.05$). Although the presence of lignin leads to a stiffer behaviour, the ductility of the composite samples is not compromised, due to the good compatibility and effective interfacial adhesion between PA6 matrix and lignin filler [37,52].

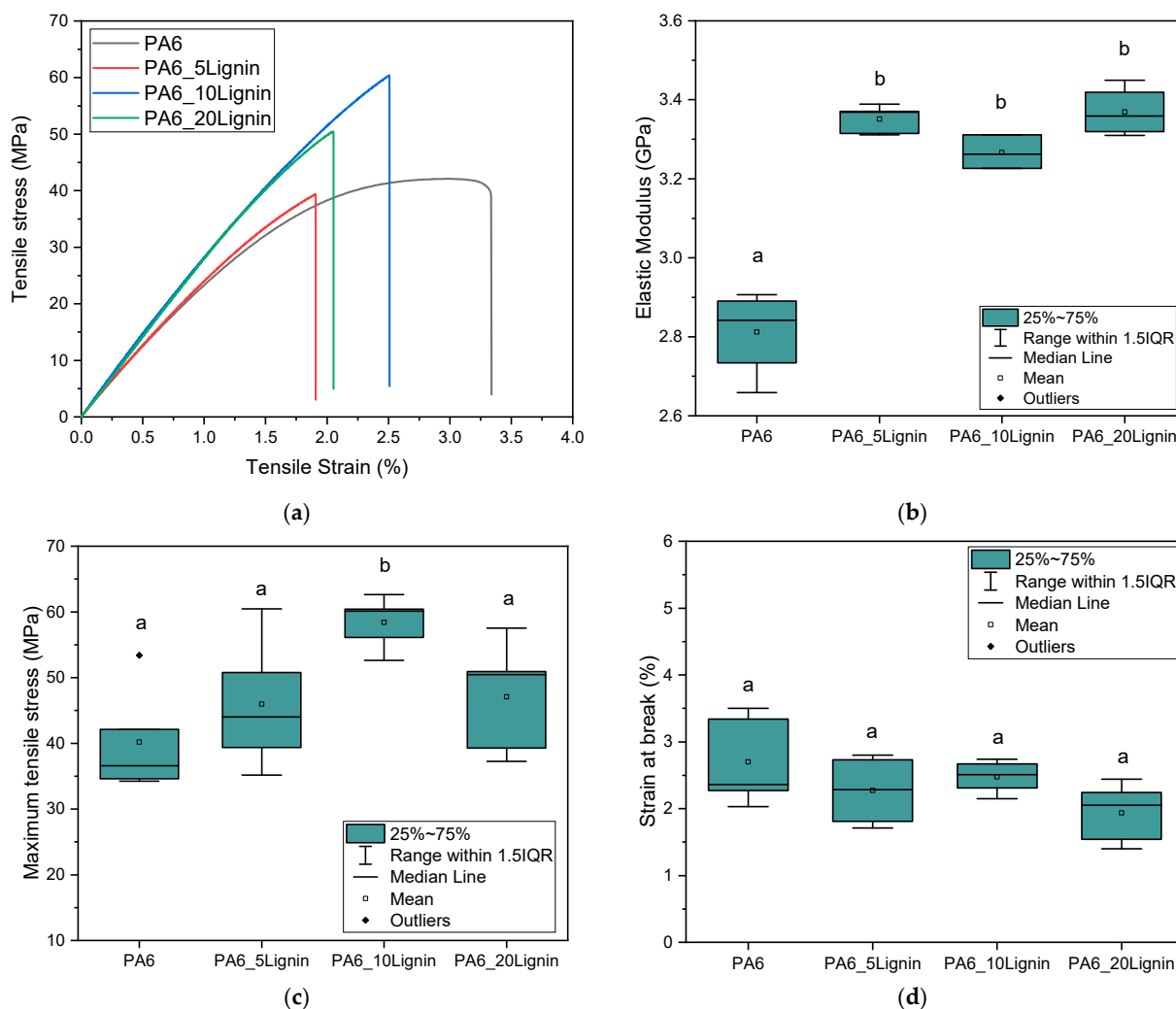


Figure 6. Results of quasi-static tensile tests on neat PA6 and the relative composites. (a) Stress–strain curves; (b) elastic modulus; (c) maximum tensile stress; and (d) strain at break. Different letters indicate that results are statistically different ($p < 0.05$).

3.7. Flame Behaviour

Figure 7 shows representative specimens from each PA6-lignin composition after the flammability test in a horizontal configuration, while Table 2 summarises the main results of these tests.

From the result of the UL-494 tests reported in Table 2 for the horizontal configuration, it has been demonstrated that all the composites exhibit a self-extinguishing behaviour, with no flame propagation observed immediately upon removal of the burner from the samples. For the vertical configuration, the neat PA6 sample is classified as V-2, primarily due to the occurrence of molten dripping during each ignition. These results are in agreement with other literature studies [53,54]. The addition of 5 wt% lignin is not sufficient to improve the flammability classification, as dripping phenomena occurred during the second ignition.

On the other hand, samples containing 10 wt% and 20 wt% of lignin achieve a V-0 rating, due to very short afterflame times and complete suppression of dripping during both ignitions. The improved vertical flammability performance at higher lignin contents can be attributed to the char-forming ability of lignin, which, due to its highly aromatic structure, promotes the formation of a protective carbonaceous layer during combustion [55,56]. As can be seen clearly from Figure 7, the volume of residual char increases significantly with the lignin content. This layer acts as a physical barrier that limits heat transfer and reduces the release of flammable volatiles [57], thus preventing the dripping of molten polymer. Overall, these findings demonstrate that lignin can serve as an effective and green flame retardant for PA6. Further analysis to deeply investigate the flame behaviour of these composites will be carried out through the Limit Oxygen Index (LOI) test and cone calorimetry.

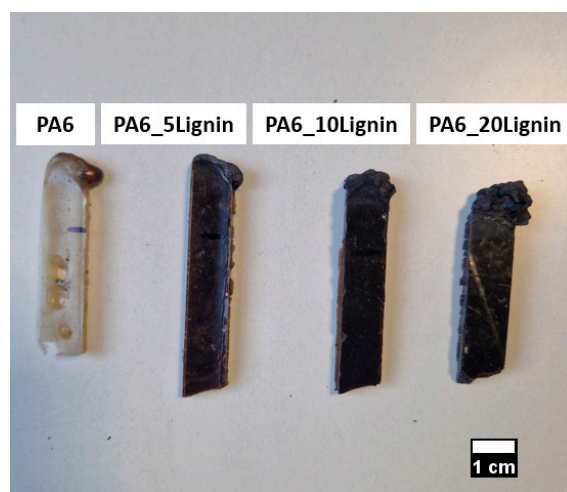


Figure 7. Representative PA6-based specimens after UL-94 tests (horizontal configuration).

Table 2. Results of UL-94 tests on neat PA6 and the relative composites.

Sample	Horizontal Configuration			Vertical Configuration	
	Burning Rate	Ranking	t_1-t_2 (s)	Dripping	Ranking
PA6	SE	HB	1–2	Yes-Yes	V-2
PA6_5Lignin	SE	HB	0–11	No-Yes	V-2
PA6_10Lignin	SE	HB	0–2	No-No	V-0
PA6_20Lignin	SE	HB	0–3	No-No	V-0

t_1 and t_2 are the afterflame times after the first and second ignition, respectively. Dripping: Yes-Yes = dripping during both ignitions; No-Yes = dripping only during second ignition; No-No = no dripping during both ignitions. SE: self-extinguishing.

4. Conclusions

This work successfully demonstrated the feasibility of using sulfonated lignin as a sustainable and multifunctional filler in polyamide 6 composites without compatibilizers or chemical modification. The primary objective of this study was to establish clear relationships between the structure and properties of these composites and to evaluate whether lignin could simultaneously enhance the thermo-mechanical performance and flamer retardancy of PA6. Rheological measurements showed higher viscosity and shear moduli with increasing lignin concentration, indicating restricted polymer chain mobility and the presence of strong physical polymer–filler interaction in the molten state. FT-IR analysis suggested the occurrence of hydrogen bonding between amide groups of PA6 and polar functional groups of lignin, which resulted in good compatibility and interfa-

cial adhesion, as confirmed by FESEM observations. DMTA evidenced the stiffening role played by lignin, showing increased storage modulus and a shift in the glass transition temperature towards higher values. Quasi-static tensile tests showed a significant increase in elastic modulus upon the addition of lignin, passing from 2.8 GPa for neat PA6 to 3.3 GPa for all lignin-filled composites. A significant improvement in tensile strength was also observed at a lignin concentration of 10 wt% (+45% with respect to neat PA6), while the ductility was not compromised. The investigation of the flammability behaviour performed through UL-94 tests highlighted a substantial improvement in vertical flame resistance with lignin contents higher than 10 wt% (V-0 classification achieved for PA6_10Lignin and PA6_20Lignin samples), due to the lignin char-forming ability.

Overall, the results of the present study confirmed that sulfonated lignin can act simultaneously as an eco-sustainable reinforcing filler and flame retardant for PA6, thereby providing a promising alternative to conventional reinforcing fillers (e.g., talc and calcium carbonate) and traditional halogenated or phosphorus-based flame retardants. The composite with 10 wt% lignin was the optimal formulation, exhibiting the best balance of thermal stability, mechanical properties and flame retardancy.

Future research will focus on exploring the use of lignin-based PA6 composites in practical applications, particularly where the demand for more sustainable and flame-resistant materials is constantly growing, such as for automotive interior parts and in buildings. In addition, long-term performance under service conditions, including thermal ageing, moisture exposure and mechanical fatigue, must be investigated to assess the durability and reliability of these materials in real environments.

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Abbreviations

The following abbreviations are used in this manuscript:

PA6	Polyamide 6
SEM	Scanning electron microscopy
TGA	Thermogravimetric analysis
DSC	Differential scanning calorimetry
FT-IR	Fourier-transform infrared spectroscopy
DMTA	Dynamic mechanical thermal analysis
HB	Horizontal burning
V	Vertical burning

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