

# Styrene/Lignin-Based Polymeric Composites Obtained Through a Sequential Mass-Suspension Polymerization Process

Priscilla Araújo Victor<sup>1,2</sup> · Sílvia Belém Gonçalves<sup>2</sup> · Fabricio Machado<sup>1</sup> 

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**Abstract** A modified sequential mass-suspension polymerization was employed to ensure adequate dispersion of lignin into the monomeric phase. Due to its complex macromolecular structure and low compatibility with styrene, eucalyptus wood-extracted lignin, via a modified Kraft method, was esterified with methacrylic anhydride to ensure organic phase homogeneity into the reaction medium. Infrared spectroscopy showed a decrease in the hydroxyl band, a characteristic of natural lignin ( $3200\text{--}3400\text{ cm}^{-1}$ ) and an increase in the characteristic ester band ( $1720\text{--}1740\text{ cm}^{-1}$ ) whereas nuclear magnetic resonance measurements exhibited intense peaks in the range from 1.7 to 2.05 ppm ( $-\text{CH}_3$ ) and 5.4 to 6.2 ppm ( $=\text{CH}_2$ ), related to methacrylic anhydride. Comparatively, the esterified lignin also displayed an increase of its glass transition temperature for  $98\text{ }^\circ\text{C}$ , related to natural lignin, whose  $T_g$  was determined to be equal to  $91\text{ }^\circ\text{C}$ . Styrene/lignin-based polymers exhibited higher average molar masses in comparison to the values observed for polystyrene synthesized with similar amounts of benzoyl peroxide, due to the ability of lignin to act as a free-radical scavenger. Composites obtained with styrene and natural or esterified lignin were successfully synthesized, presenting regular morphology and proper lignin dispersion. Based on a very simple polymerization

system, it is possible to enhance the final properties of polystyrene through the incorporation of lignin, which represents an important platform for developing attractive polymeric materials from renewable resources.

**Keywords** Styrene · Lignin · Polymer composites · Sequential mass-suspension polymerization

## Introduction

Environmental issues have never been discussed as of late, with a central point in sustainable development as an attempt to provide for the population's needs today without affecting future generations. With an increased consumption, an increase in the amount and variety of waste generated, and augment in specific biomass waste has been a reported problem for the environment, especially when the disposal or storage is done incorrectly. To minimize the inappropriate disposal of these materials, an alternative method is to turn what would be "garbage" in to raw material for the production of new polymeric materials [1–3].

The polymers have gained special prominence in recent decades by displaying numerous properties of technological interest such as mechanical and chemical resistance, low density, durability, thermal and electrical insulation, among others. In the quest for improved mechanical and thermal properties of polymers, it is common to incorporate inorganic or organic fillers, micro or nanoparticulate, or elastomeric phases of organic polymers for the purpose of producing composites or nanocomposites with different properties [4].

Polystyrene (PS) is one of the highest *commodity* polymers produced in the world, and is mainly synthesized through radical polymerization by using heterogeneous

✉ Sílvia Belém Gonçalves  
silvia.belem@embrapa.br

✉ Fabricio Machado  
fmachado@unb.br

<sup>1</sup> Instituto de Química, Universidade de Brasília,  
Campus Universitário Darcy Ribeiro, CP 04478,  
CEP 70910-900 Brasília, DF, Brazil

<sup>2</sup> Embrapa Agroenergia, Parque Estação Biológica, PqEB s/n°,  
W3 Norte, CEP 70770-901 Brasília, DF, Brazil

polymerization processes, such as suspension and emulsion. Despite the high global production and their peculiar features, such as high glass transition temperature, gloss, hardness, high refractive index and stiffness, the *railings* the production of styrene-based polymeric materials has as great challenge to obtain polystyrenes less fragile and brittle, which corresponds to its main disadvantage [1].

Lignin is formed by three-dimensional macromolecules of phenylpropane origin, and represents about 30% of its biomass, which mostly lies in dark regions of the timber. The structure can be studied by its decomposed products, which expresses an elemental composition of 53–65% carbon, 6–9% hydrogen and 26–36% oxygen. In its natural form portrays no sulfur, phosphorus, nitrogen or other elements [5, 6]. There are different methods of separating lignin, to which none achieve the lignocellulosic components as its found in nature. There will always be influences of the extraction processes. The main objective is the separation of lignin from other fibrous components [7].

Lignin, from the view that its nature is not soluble in most organic solvents, rather is soluble in an aqueous base at high temperatures, and stable in mineral acid solutions. The chemical modification of lignin aims to increase its hydrophobicity, and consequently facilitate their dispersion in organic solvents [8, 9]. The increased in the carbon aliphatic chain performed via replacing hydroxyl groups per ester groups on lignin, can reduce its polarity and increase its solubility in nonpolar solvents. The modification by introducing double bonds with maleic anhydride or methacrylic causes a reduction in glass transition temperature of the lignin, which significantly increases its solubility in organic solvents. This allows modification of the mechanical properties when dispersed in polymeric matrices [10–13]. These components are most commonly utilized during this modification can be acetic anhydride, propionic, butyl, maleic and methacrylic. Among these modifications performed in lignin with methacrylic anhydride is the most attractive in the use of polymerization reactions via free radicals [14].

There are a wide variety of acid anhydrides that allow the addition of side chains to achieve solubility in various solvents. In these reactions, there are more effective other catalysts. For example, 1-methylimidazole is 400 times more reactive than pyridine for reactions with anhydrides [10, 15–17]. Recently, Holmberg et al. [18] developed lignin-based methacrylate polymers exhibiting tunable thermal and viscoelastic properties. According to the authors, lignin-based heteropolymers presented composition-dependent glass transition temperature and component-dependent thermal degradation temperatures.

Jiang et al. [19] evaluated the in situ dispersion and compatibilization of lignin with epoxidized natural rubber through a high-temperature dynamic heat treatment,

leading to the formation of composites with improved mechanical properties. Hilburg et al. [20] synthesized nanocomposites based on methyl methacrylate and styrene hopolymers grafted from kraft lignin through atom transfer radical polymerization (ATRP). It was observed for all nanocomposites that both the glass transition temperatures and toughness increased, but the modulus decreased in comparison with homopolymers. Shah et al. [21] also evaluated the production of poly(methyl methacrylate)/lignin composites by ATRP. It was showed that mechanical properties of the composites were significantly improved due to the tethering of polymeric chains to the surface of lignin, which indicates the efficient interaction between poly(methyl methacrylate) and lignin.

The use of lignin to produce carbon fibers has shown promise in applications as electrodes because the bonds between the fibers improve the electrical properties of the material, increasing its electrical conductivity and of Kraft lignin-based carbon fibers produced by electrospinning. This attractive material has a potential to replace electrodes in batteries, solar cells, and capacitors. The technique used to produce lignin-based carbon bonded fibers also showed an increase in tensile strength due to bonding between the fibers [22].

In the field of biomedicine, lignocellulosic materials might be employed for the development of nanostructured composites intended for targeting drug delivery and tissue engineering and regeneration applications. As additional and important features, lignin exhibits antioxidant capacity and may demonstrate antiviral activity against human immunodeficiency virus and other anti-microbial activities. The combination of conducting polymers with lignin allows for the production of antioxidant materials capable of reducing the oxidative stress of the surrounding biological tissue [23].

Lignin (or chemically modified lignin) can be combined with a wide variety of both natural and synthetic polymer matrices. In a recent literature review, Kun and Pukánszky [24] have explored the use of lignin-based materials as stabilizing agent, dispersed into thermoplastic matrices of polyolefins, such as, poly(ethylene-co-vinyl alcohol), polypropylene, polyethylene and their copolymers. As stated by the authors, due to the presence of phenolic OH groups, lignin was able to scavenge free radicals, presenting antioxidant action. For this reason, it is expected that lignin effect of lignin on the polymer is twofold: (i) stabilizer, improving thermal properties and avoiding degradation during polymer processing; and (ii) protection of the thermoplastic matrix against oxidation. The use of modified lignin has also been explored with aromatic polymers, showing that lignin modified with maleic anhydride improved interactions of lignin with polystyrene, enhancing its compatibility when compared to unmodified lignin.

This work presents as main advantages the use of combined mass-suspension processes, which allows for the proper dispersion of both the natural and modified lignin microparticles. It is important to keep in mind that the chemical modification of lignin with methacrylic anhydride enables free-radical copolymerization of the esterified lignin with styrene, avoiding the undesired lixiviation problem of lignin from the thermoplastic polystyrene matrix during both the polymerization reaction and the polymer processing. The incorporation of lignin is also beneficial, as it may enhance the thermal properties and it can protect the polymer against oxidative degradation. So, the present work displays as its main objective the development of new classes of polymeric materials obtained by polymerizing styrene with natural and esterified lignin by using a sequential mass-suspension polymerization. Furthermore, a projection of the incorporation of lignin *in nature* polystyrene matrix coupled with *in situ*, performed in sequential polymerization process of mass-suspension type. It is important to emphasize that this work used material from biomass, which is usually burned to generate energy or disposed of as waste. The generated product is incorporated into a synthetic polymer matrix, which made it possible to replace up to 20% of a synthetic material lignin, an abundant and renewable material.

## Experimental

### Materials

In the performed research, Eucalyptus wood samples belonging to the species *Eucalyptus grandis* (which is resultant of crossing germinating *Urograndis* and *Urophylla*) of approximately for five years, comminuted in a rotary knife cutter Willey Star FT-60 (Fortinox, Piracicaba, Brazil).

In the determination of lignin content, sulfuric acid ( $\text{H}_2\text{SO}_4$ ), consisting of a purity of 98%, was supplied by JT Baker (New Jersey, USA) was used. Distilled water was also used.

During the extraction of lignin, the alkaline sodium hydroxide (NaOH), with a 99% purity supplied in microbeads by VETEC Química Fina Ltda (Rio de Janeiro, Brazil), and hydrochloric acid (HCl) of 37% PA purity, supplied by Fluka (New York, USA) and distilled water.

In the polymerization reactions, styrene was used, with a purity of 99%, supplied by Spectrum (California, USA); benzoyl peroxide (BPO LUPEROX 78), with a purity of 75% containing 25% of water as a stabilizer and active oxygen of 5% was kindly donated by Arkema Química Ltda (São Paulo, Brazil); poly(vinyl alcohol) (PVA DENKA Poval B-24), with a degree of hydrolysis

in the range of 86–89% and a purity of 99% was kindly donated by Denka (Tokyo, Japan); sodium dodecylsulfate, supplied by Quimibrás Indústrias Químicas SA (Rio de Janeiro, Brazil); hydroquinone, supplied by Merk (São Paulo, Brazil); and distilled water.

The esterification process of lignin was performed with the following reagents: 1-methylimidazole in 99% purity, and methacrylic anhydride with 94% purity were supplied by Sigma-Aldrich Brasil Ltda (São Paulo, Brazil); 1–4 dioxane with 99% purity, diethyl ether with 99.5% purity and cyclohexane 99% purity were supplied by VETEC Química Fina Ltda (Rio de Janeiro, Brazil); and deionized water.

For the analysis of  $^1\text{H}$  NMR, deuterated dimethyl sulfoxide (DMSO) was used, consisting of 99.9% purity, and was provided by the Sigma-Aldrich Brasil Ltda (São Paulo, Brazil). All chemicals were used as received without additional purification.

## Methods

### *Determination of Lignin Content in Wood*

For the determination of lignin in eucalyptus wood, the Klason method was utilized, as described by Gouveia et al. [25] In accordance with this method, 1 g comminuted eucalyptus wood was pretreated with 5 mL of sulfuric acid 72% v/v, under vigorous stirring for 7 min at 45 °C in a constant temperature bath. Then the mixture was transferred to a 250 mL Erlenmeyer flask, adding a volume of 125 mL of distilled water, which was autoclaved for 30 min at 121 °C/1 atm. After cooling, the solid fraction was filtered on filter paper. The material retained on the filter was washed with 2 L of distilled water, and subsequently dried in an oven at 100 °C. The sample was then calcined to determine ash amount. From the data obtained, it was possible to determine the percentage of insoluble lignin in relation to the initial sample mass.

### *Extraction of Lignin by Using the Modified Kraft Method*

In modified Kraft method for cooking, 15% NaOH was used in proportion of 5 mL/1 g of milled wood. The solution was autoclaved for 1 h at approximately 120 °C/2 atm. After cooking, the solution was filtered and washed with hot water. The filtrate rich in lignin, which was called black liquor, was treated with a 10% HCl solution for precipitating lignin. The lignin solution was separated in a refrigerated centrifuge and dried in an oven at 50 °C [26].

### Sequential Mass-Suspension Polymerization Process

The sequential mass-suspension polymerization reactions were performed in a borosilicate glass jacketed reactor, containing a 250 mL capacity, and equipped with a condenser coupled with cooling water ( $20^{\circ}\text{C} \leq T \leq 25^{\circ}\text{C}$ ) and overhead mechanical stirrer RW 20 digital (IKA® Works, Inc., São Paulo, Brazil) coupled to a helix-type impeller to ensure the proper agitation of the reaction mixture [27].

Before the sequential mass-suspension polymerization process, with a goal of increasing the compatibility between the natural (N.B. throughout the text, natural lignin is used to represent the lignin obtained by using a modified Kraft method) or esterified lignin and styrene, a conditioning stage was carried out; a previous contact between the constituents of the polymerization reaction was carried out for 12 h under vigorous stirring at room temperature [27].

The polymerization was carried out in two main steps, according to the following sequence: (i) *mass polymerization*, is characterized by dispersion of the natural lignin or esterified lignin with average diameter of approximately  $75\ \mu\text{m}$  in styrene. The reaction was maintained under constant agitation of 1000 rpm at  $85^{\circ}\text{C}$  until 50–60% conversion was achieved (approximately 2 h). Polymerization reactions were performed with natural lignin (or esterified lignin) ranging from 0 to 20% related to styrene (58 g) and benzoyl peroxide lying in the interval from 2 to 9 g; (ii) *suspension polymerization*, which is characterized by the addition of a PVA solution (135 mL with concentration in the range from 5 to 50 g/L) in a viscous reaction medium (from first stage of polymerization) while the agitation is decreased to 500 rpm. This process was maintained for 4 h and  $85^{\circ}\text{C}$ . At the end of the reaction and after cooling to room temperature, the reaction mixture was filtered and the recovered polymer particles were washed with sodium dodecyl sulfate and hydroquinone solutions, in order to remove residual suspending agent and monomers, and to inhibit the continuing of the reaction. Then the material was dried in an oven at  $50^{\circ}\text{C}$ .

As a matter of fact, in both the bulk and suspension polymerization processes, the stirring speed of the reaction medium guarantees the uniform dispersion of the reaction mass and favors the heat distribution, avoiding the

undesirable overheating phenomenon. In the particular case of suspension polymerization, the average particle size and particle size distribution are strongly dependent on both the stirring speed and the concentration of the suspending agent [28, 29].

### Determination of Total Hydroxyl

Natural lignin (10 mg) was dissolved in 25 mL of 1,4-dioxane and transferred to 100 mL flasks. The first sample was adjusted to pH 1 using 1 M HCl, and the other sample was adjusted to pH 13 using 1 M KOH, and the volumes was completed with a solution of water/1,4-dioxane (1:1 v/v). The spectrum in the 250 nm region was obtained using the solution to pH 1, and the reference solution having pH of 13 as a sample. The same procedure was repeated for the esterified lignin [30].

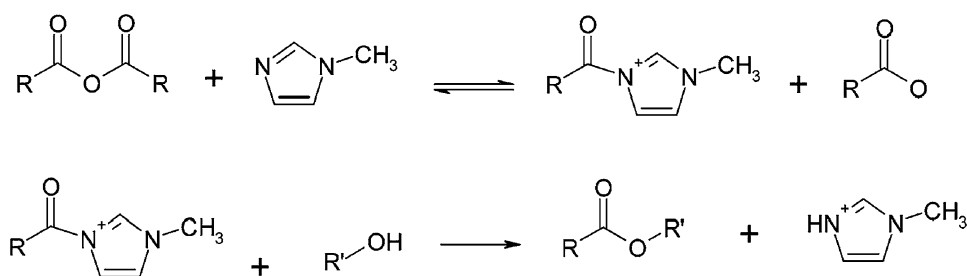
### Chemical Modification of the Natural Lignin

The chemical modification of lignin was performed based on the experimental method described by Thielemans and Wool [31]. Scheme 1 illustrates the esterification reactions, where the methacrylic anhydride reacts with the 1-methylimidazole forming the *N*-alkyl-*N'*-methylimidazolium ion, which reacts irreversibly with the alcohol group of the natural lignin forming ester [31, 32].

The esterification reaction was carried out at  $50^{\circ}\text{C}$  under an atmosphere of nitrogen (with the goal of avoiding the oxidation of lignin) and vigorous stirring. The reaction was left for 24 h to ensure a better conversion. The reaction mixture consists of 6.1 mL of a mixture of methacrylic anhydride and 1-methylimidazole (60:1) and 4 mL of 1,4-dioxane for each gram of natural lignin.

After 24 h, the of reaction, diethyl ether was added to stop the reaction. Subsequently, the mixture was washed three times with deionized water. The aqueous phase was filtered to remove all catalyst. The cyclohexane was subsequently added to separate the esterified lignin. The precipitate was recovered by vacuum filtration and dried in a vacuum oven at  $60^{\circ}\text{C}$  for 24 h. The quantities used were in the final process for each 100 mL of the reaction mixture, 200 mL of ethyl ether, 600 mL ( $3 \times 200\ \text{mL}$ ) of

**Scheme 1** Esterification reaction of lignin with methacrylic anhydride using 1-methylimidazole as catalyst [31, 32]. Reprinted with permission from reference [31]. Copyright © 2005, American Chemical Society



deionized water and 200 mL of cyclohexane. The reduction of cyclohexane also reduces the recovery yield of lignin esterified [31].

#### *Solubility Test of Lignin in Styrene*

Styrene (1 g) and natural lignin (0.05 g) were placed in a test tube and immersed in an oil bath at 85 °C for 1 h. After this period, the solution was removed from the bath and allowed to precipitate. Then, the supernatant was carefully removed and the pellet was allowed to dry. After 24 h, the tubes were weighed again to verify the amount of natural lignin which was not soluble in styrene. The same procedure was repeated for the esterified lignin [31].

### **Characterization Techniques**

#### *Infrared Spectroscopy (IR)*

The infrared spectroscopy analysis of natural lignin and esterified lignin were conducted in attenuated total reflectance (ATR) accessory on a FT-IR spectrometer (Spectrum Two, PerkinElmer, USA) with the resolution of 4 cm<sup>-1</sup> and average of 32 scans.

#### *Nuclear Magnetic Resonance (NMR)*

About 25 mg natural lignin were dissolved in 1 mL of deuterated dimethyl sulfoxide (DMSO), and the NMR spectra were acquired on Bruker NMR spectrometer (Ascend™ 600 MHz, USA), equipped with 5 mm probe operating at 600 MHz and the spectra were acquired at 25 °C using TMS as internal standard. The same procedure was repeated for the esterified lignin.

#### *Thermogravimetric Analysis (TGA)*

Thermogravimetric analyses were carried out on a thermogravimetric analyzer Shimadzu DTG-60H model (Shimadzu Scientific Instruments, Maryland, USA) with inert atmosphere of N<sub>2</sub> with flow of 30 mL/min at heating rates of 10 °C/min and temperature range between 30 to 800 °C. Measurements were performed by using around 8.0–10.0 mg of the material weighed into platinum crucibles.

#### *Differential Scanning Calorimetry (DSC)*

DSC analyses were performed on a Shimadzu DSC-60 calorimeter (Shimadzu Scientific Instruments, Maryland, USA), with approximately 8 mg of material were sealed aluminum crucibles at heating rates of 10 °C/min, under helium atmosphere with a flow rate of 30 mL/min and

temperature range of –30 to 250 °C for both natural lignin and esterified lignin and a range of –30 to 190 °C for the polymer samples.

#### *Scanning Electron Microscopy (SEM)*

The morphology of the natural lignin, esterified lignin and formed polymers were determined by Scanning Electron Microscopy (SEM) on a JEOL JSM-7001F Field Emission Scanning Electron Microscope (Jeol Ltd., Tokyo, Japan) operating at an accelerating voltage of 15 keV. The samples were placed on stubs and metallized with gold.

#### *Light Microscopy*

The morphology of natural lignin and esterified lignin formed polymers that were also analyzed by light microscopy light microscope Carl Zeiss Axio Imager.A2 (Carl Zeiss Microscopy, USA).

#### *Viscosimetry*

The viscosity of polymeric materials was evaluated on a Brookfield rheometer/viscometer equipped with a Thermosel and spindle SV-34, where approximately 12 g of the polymer were analyzed for 25 min, at 180, 190, 200 and 210 °C.

#### *Gel Permeation Chromatography (GPC)*

GPC measurements were carried out on a Viscotek RImax (Malvern Instruments Ltd., Worcestershire, United Kingdom) equipped with inline degasser, pump, autosampler, oven, refractometer detector, injection loop of 100 µL and columns KF-802.5, KF-804L e KF-805L installed in sequence, all compatible with the solvent tetrahydrofuran (THF) used as mobile phase. The calibration curve was built using standard polystyrene samples with mass-average molar mass ranging from 1.2 × 10<sup>3</sup> to 4.5 × 10<sup>6</sup> and molar-mass dispersity close to 1.0. GPC measurements were performed at 35 °C using THF as mobile phase at a flow rate of 1 mL/min.

## **Results and Discussion**

### **Determination of Lignin Content in Wood**

The lignin content in eucalyptus wood determined according to the method described by Gouveia et al. [25] was about 28.93 ± 0.26%, whose experimental result is in accordance with that described in the literature normally found in the range between 25 and 30%.



## Extraction, Esterification and Characterization of Lignin

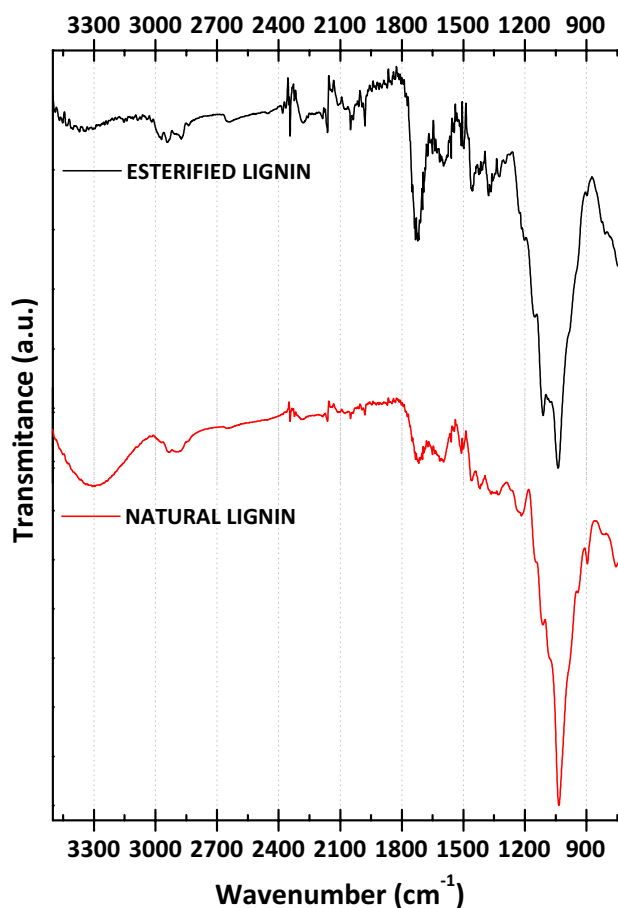
By using the modified Kraft process, it was possible to obtain a yield of approximately 50%. This observed value agrees very well with the amount of lignin reported elsewhere [26]. Yields observed in the extraction experiments can also be attributed to losses during the process of filtration and washing.

The esterification process had targeted the hydroxyl groups (OH) in the natural lignin, aimed at replacing the hydroxyls by agents with double-bonds functionality to increase reactivity in radical polymerization. The addition of double-bonds functionality through the esterification of lignin hydroxyl groups with methacrylic anhydride presents twofold advantage: (i) can increase its solubility in styrene [10] and (ii) allows for the free-radical polymerization between esterified lignin and styrene, leading to a proper dispersion of the modified lignin into the thermoplastic matrices of polystyrene.

The hydroxyl content determined in natural lignin was approximately  $5.7 \pm 0.006$  wt%. (N.B. According to the literature the hydroxyl content in lignin may vary in the interval from 8 to 11 wt% [33]). This process was needed to establish a good proportion between the reactants, so that the esterification reactions conducted were using about 6 mL of methacrylic anhydride for each gram of lignin. In the esterification process using lignin methacrylic anhydride, it was possible to recover approximately 64% of the mass lignin.

After the esterification process, the experiment was repeated in order to determine the hydroxyl content still present in the esterified lignin. The hydroxyl content and substitution percentage which was determined that esterified lignin was about 1.55 wt%, with a content of hydroxyl substitution of 72.8%. This replacement content can be explained by the steric hindrance occurring within the lignin structure.

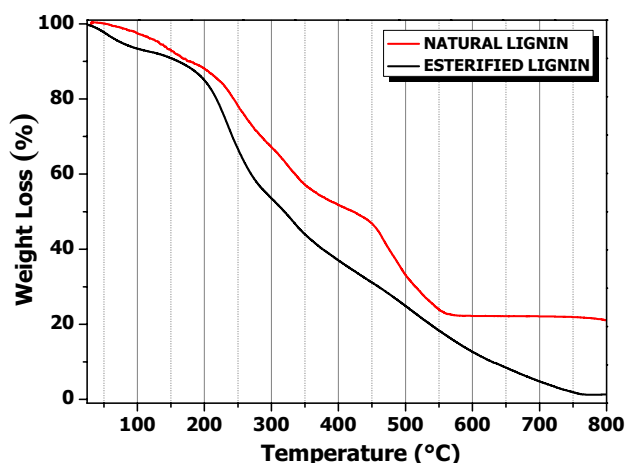
In the characterization by means of Infrared Spectroscopy, the natural lignin spectrum of interest ranges from 700 to 4000  $\text{cm}^{-1}$ , which is used for identifying functional groups and typical lignin bonds. The stretches of groups such as of syringyl and guaiacyl ring may be observed at 1325 to 1330  $\text{cm}^{-1}$  and 1270 to 1275  $\text{cm}^{-1}$ , respectively. Other typical natural lignin range between 3200 and 3400  $\text{cm}^{-1}$  is characteristic of a high concentration of hydroxyl, and about 1100  $\text{cm}^{-1}$  characteristic of secondary alcohols, as shown in Fig. 1. Table 1 shows the main absorption peaks shown in characteristic infrared spectrum of eucalyptus wood lignin. The values obtained in this study are similar to those found in the literature [26, 34, 35].



**Fig. 1** IR Spectrum of the natural and esterified lignins extracted from *Eucalyptus grandis* through a modified Kraft method

**Table 1** Characteristic absorption bands of lignin

Absorption range ( $\text{cm}^{-1}$ )	Assignment
3400–3200	OH stretch
2940–2820	CH stretch methyl group and/or methylene
1740–1720	Stretch C=O unconjugated ketone and ester group
1715–1710	C=O stretch the unconjugated aromatic ring
1585–1580	Ring vibration combined with an $\alpha$ carbonyl group
1515–1505	Aromatic ring vibration
1470–1460	Deformations asymmetric CH
1430–1425	Aromatic ring vibration
1420–1425	CH bonds of methyl groups
1370–1365	Deformations symmetric CH
1330–1325	Stretch syringyl ring
1270–1275	Stretch guaiacyl ring
1268–1270	Stretch aromatic CO (methoxyl)
1230–1215	Stretch CO aromatic (phenyl)
1130–1120	Deformation (in the plan) CH (in siringylic syringyl unit)
1100–1030	CH deformations in the plane in guaiacyl unit and CO in secondary aliphatic alcohols and ethers



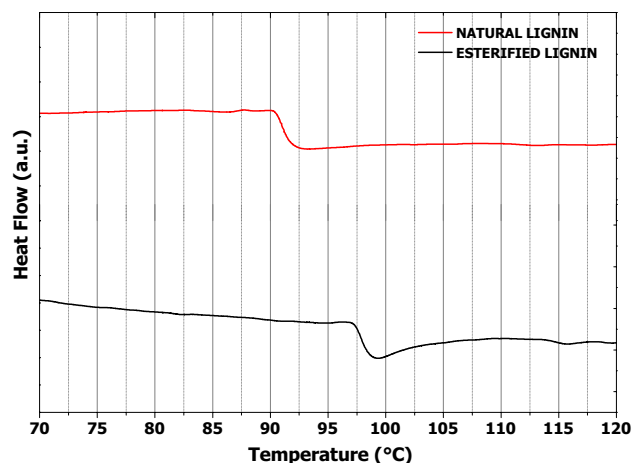
**Fig. 2** Thermal stability of natural and esterified lignins extracted from *Eucalyptus grandis* through a modified Kraft method

In the analysis of esterified lignin (Fig. 1), when compared to the natural lignin, a decrease in characteristic hydroxyl band ( $3200\text{--}3400\text{ cm}^{-1}$ ) coupled by an increase in the band characteristic of esters ( $1720\text{ to }1740\text{ cm}^{-1}$ ). The intense band at  $1100\text{--}1030\text{ cm}^{-1}$  is characteristic of guaiacyl units and ethers (Table 1).

The thermal decomposition of natural lignin results from complex reactions characterized by different stages of weight losses. In the TGA curve (Fig. 2), the weight loss at temperatures between  $90\text{ and }110\text{ }^{\circ}\text{C}$  is mainly due to evaporation of water and low molecular weight substances such as carbon monoxide and carbon dioxide. The weight loss at  $200\text{ }^{\circ}\text{C}$  refers to the beginning of the pyrolysis reaction of natural lignin. The natural lignin degradation process usually occurs above  $300\text{ }^{\circ}\text{C}$  [36], which breaks the linkages between units resulting in the loss of phenols, which are assigned. Aromatic rings, characteristic of the natural lignin, are degraded in temperatures above  $400\text{ }^{\circ}\text{C}$ .

In the thermal decomposition of esterified lignin described by TGA curve (Fig. 2), significant differences were observed as compared to the natural lignin, showing that the esterification reaction led to a decrease in thermal stability with decomposition temperatures: between  $200\text{ and }300\text{ }^{\circ}\text{C}$  with degradation of approximately 50%, compared to only 42% of the natural lignin; between  $300\text{ and }550\text{ }^{\circ}\text{C}$  with degradation of approximately 80%, against 75% of the natural lignin; and temperature above  $550\text{ }^{\circ}\text{C}$ , the degradation is approximately 98% of esterified lignin.

The natural lignin exhibits an amorphous structure and its glass transition temperature ( $T_g$ ) varies depending on the source and type of extraction process, which is usually between  $85\text{ and }120\text{ }^{\circ}\text{C}$  [37]. The amount of water and molecular weight of the natural lignin also affect its  $T_g$ . Figure 3 shows that the glass transition temperature of the natural lignin occurs at  $91.2\text{ }^{\circ}\text{C}$ , whereas the  $T_g$  of



**Fig. 3** Thermogram of the natural and esterified lignins extracted from *Eucalyptus grandis* through a modified Kraft method

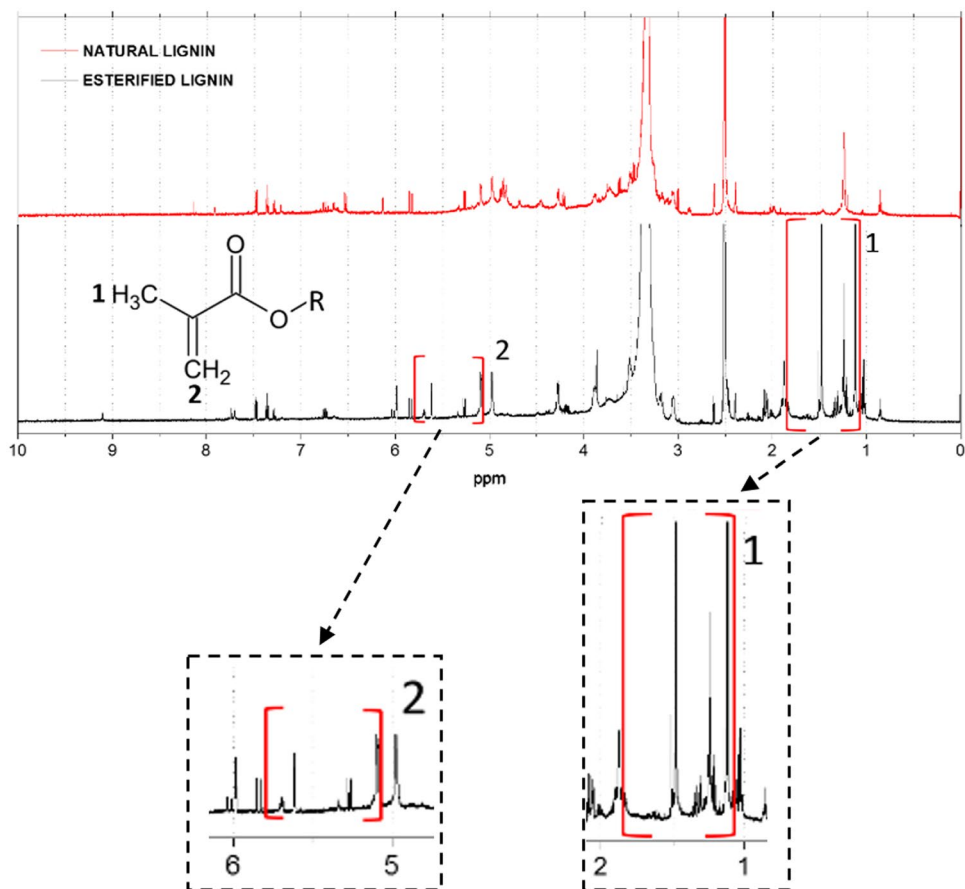
the esterified lignin was determined equal to  $97.9\text{ }^{\circ}\text{C}$ . The increase in the  $T_g$  value of the esterified lignin can be attributed to the substitution of the OH groups by larger groups, causing reduction in mobility of the lignin chains.

NMR analysis of the natural lignin aimed at evaluating the different hydrogen protons present in the natural lignin, such as those related to aliphatic chains, aromatic rings and hydrogens methoxylic, aliphatic and phenolic [26, 33]. The  $^1\text{H}$  NMR spectrum provides important information regarding the hydroxyl groups present in the natural lignin molecule. The main signals are: 2.02 ppm, characteristic of aliphatic acetate protons of aliphatic hydroxyls, 2.16 and 2.29 ppm, regarding to the protons of aromatic acetate of phenolic hydroxyl and 3.82 ppm relative to methoxylic hydrogen atoms. According to Fig. 4, it is possible to observe the  $^1\text{H}$  NMR spectrum of the natural lignin. Table 2 shows the assignments of the signals of the hydrogen NMR spectrum  $^1\text{H}$ . The main peaks of interest present after esterification of lignin are ( $-\text{CH}_3$ ) 1.7 to 2.05 ppm, and ( $=\text{CH}_2$ ) 5.4 to 6.2 ppm, featuring methacrylic anhydride, which can be observed in Fig. 4.

Samples of natural lignin present an average size within the range between  $25\text{ and }150\text{ }\mu\text{m}$ , as observed by scanning electron microscopy (Fig. 5). The morphology of the esterified lignin was also evaluated through SEM, as illustrated in Fig. 6. It is observed that, after esterification, there were the appearance of particles smaller than  $10\text{ }\mu\text{m}$ .

After the esterification was carried out, a solubility test was performed. There was a significant increase in the solubility of the esterified lignin in relation natural lignin. The solubility of natural lignin styrene is approximately 8%, as esterified lignin is about 38%. It is very important to emphasize that an increase in solubility leads to the formation of more homogeneous polymer particles, and also a better incorporation of the lignin increasing the

**Fig. 4**  $^1\text{H}$  NMR spectrum of the natural and esterified lignins extracted from *Eucalyptus grandis* through a modified Kraft method



**Table 2** Assignment of the main signals of the  $^1\text{H}$  NMR spectrum of the lignin

Chemical shift (ppm)	Assignment
2.00–2.02	( $\text{CH}_3$ -) acetates of aliphatic protons
2.16–2.29	( $\text{CH}_3$ -) phenolic protons hydrocarbon
2.59–2.61	(H) $\alpha$ $\beta$ structures of $\beta$ -
3.82–3.87	( $\text{CH}_3\text{O}$ ) protons in methoxy groups
4.23–4.26	(H) $\gamma$ in various structures

conversion of the polymerization reaction. The solubility of esterified lignin reported here is relatively below of values reported in literature, which is approximately 55% [31]. Despite this, the solubility value of esterified lignin cannot be considered as a disadvantage, as the sequential mass-suspension polymerization potentiates the incorporation of lignin, as the first step of the reaction (mass polymerization) ensures good dispersion of particulate lignin. It is also important to emphasize that methacrylic anhydride was used strategically to give esterified lignin the ability to combine chemically with styrene via copolymerization reaction.

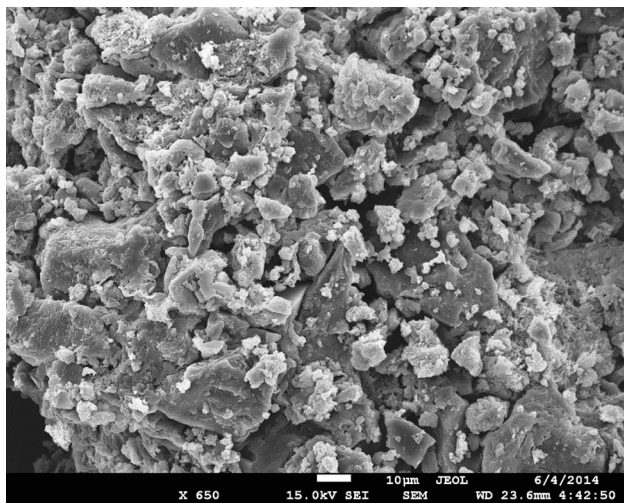
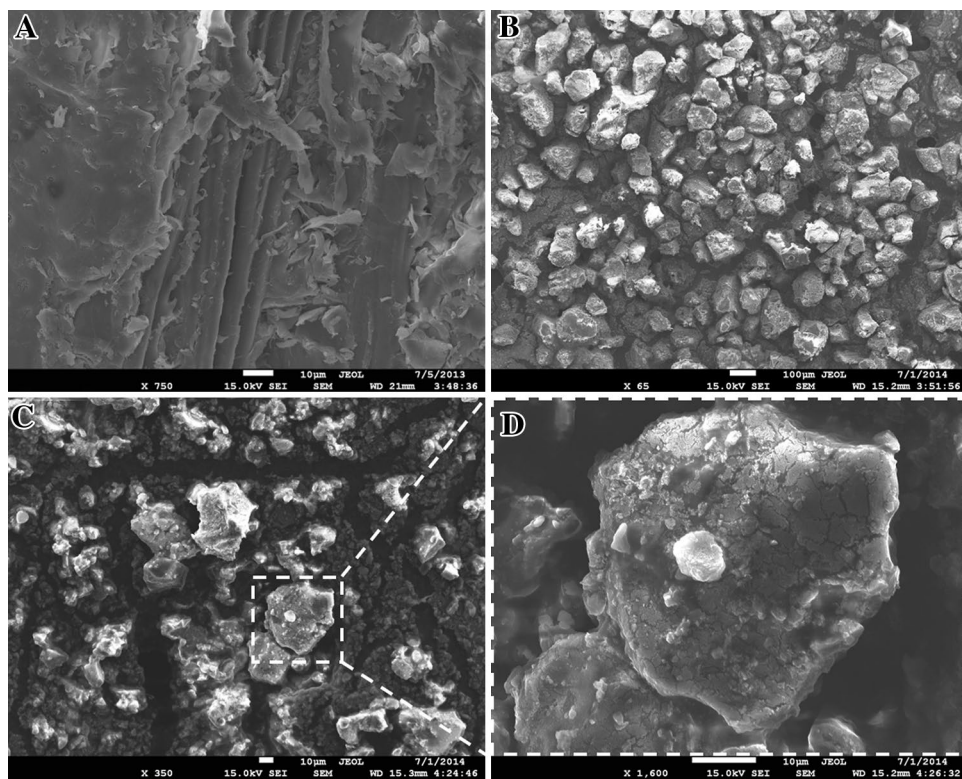
### Mass-Suspension Polymerization with Styrene and Natural Lignin

The polymer composites were formed from lignin with an average size of 75–100  $\mu\text{m}$  and styrene. Figure 7 shows a typical conversion curve of styrene in the mass polymerization process, fundamental to the determination of the ideal reaction time to the addition of the PVA aqueous phase to the highly viscous reaction medium, which characterizes the beginning of the second phase of the polymerization process. The mass polymerization stage plays a key role on the final properties of the polymer microparticles, as it improves the dispersion of microparticulate lignin in the reaction medium in the beginning of polymerization, guarantying the proper encapsulation of lignin by the growing polystyrene chains and reducing the undesirable effect of segregation between the monomer and lignin, which is normally observed when the suspension polymerization process is employed, resulting in poor incorporation of the lignin.

The reaction time of the first polymerization stage, regarding to the mass process, is closely related to viscosity of the reaction medium, being directly proportional to the reaction conversion, in a such way that, the higher the

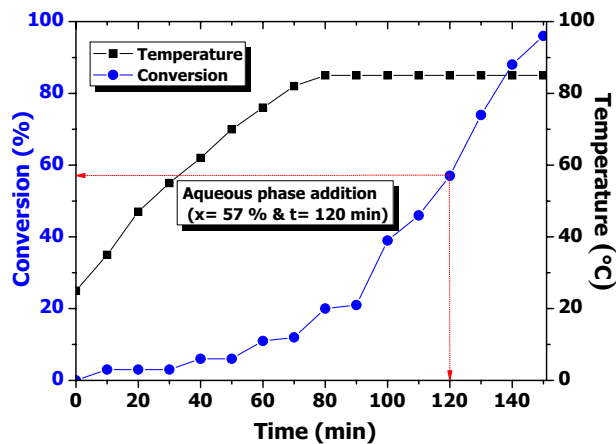


**Fig. 5** SEM image of **a** eucalyptus wood (*Eucalyptus grandis*) and **b–d** natural lignin extracted from *Eucalyptus grandis* through a modified Kraft method



**Fig. 6** SEM image of esterified lignin extracted from *Eucalyptus grandis* through a modified Kraft method

styrene conversion, the higher the viscosity of the reaction mixture. For this particular reaction system, it is convenient to work with conversions between 30 and 60%. Furthermore, the time of 120 min was chosen because the conversion is around 57% to ensure a proper lignin encapsulation by the growing polymer chains. Importantly, this reaction time and reaction conversion were chosen because the observation that the addition of PVA aqueous phase



**Fig. 7** Conversion and temperature profiles of the mass styrene polymerization carried out in batch mode

into a reaction medium with conversion below 30% results in a poor incorporation of lignin and a reaction conversion above 60% will lead to the instability of the polymerization due to the high viscosity of the reaction medium, resulting in the coalescence of the polymer particles. According to our experimental observation, the PVA solution should be added to the reaction system, under high shear, when the reaction conversion is around 57%, which is linked to a reaction time of 120 min. Sequential mass-suspension polymerization process was chosen with the idea to

increase the amount of lignin in the polymer matrix, and to facilitate the handling of the polymer produced.

From this point (addition of PVA aqueous phase), the reaction assumes a typical behavior of classical suspension polymerization. In the first stage of this process, it is the most important, because there is low compatibility between styrene and lignin. The first step provides a better contact between the reactive species by increasing the incorporation of the lignin polymer in the polystyrene matrix, and minimizes the undesirable effect of low solubility of lignin after the addition of the PVA solution. Table 3 shows the experimental conditions of all the reactions with 5, 10 and 20% lignin and their conversions.

In the polymerization reactions performed with 5% lignin, the first step included the mechanical stirring at 1000 rpm, followed by the second step at 500 rpm. This experiment expressed a conversion of 97.7%, and the images showed a good incorporation of the lignin polymer (Experiment 6, Fig. 8) with average particle diameter of approximately 220  $\mu\text{m}$  and full range lying in the interval from 100 to 340  $\mu\text{m}$ . One can observe a morphological structure of the polymer particles exhibiting macrocavities with spherical and regular morphology. The macrocavities are formed due to the accumulation of water microdroplets within the polymer particles, which is released during the reaction and during the drying process, leaving empty spaces before filled with water.

The sectioned particle shown in Fig. 8a–b was cut by microtomy, illustrating a small fragment of lignin into the polystyrene thermoplastic matrix. This observation indicates that initial structure of lignin is broken due to the development of mechanical stresses caused by the polymer production within the lignin particles associated to the growing polymer chains.

In the polymerization reactions of 10% lignin, the same behavior is observed (see Fig. 9). However, to minimize the undesirable effect of oxidation of lignin during the polymerization and stability of the reaction medium (N.B. is it

well-known that the BPO is a strong oxidant agent [38, 39], and during the polymerization a portion of the initiator is not available for styrene polymerization, leading to low conversions.), the concentration of PVA in the reaction with 10% lignin was increased to 7 g/L and the amount of BPO was also increased to 4.07 g (6.0 wt%). The result was a high polymerization yield with conversion 97.8%, good stability with polymer particles exhibiting regular, spherical morphology and homogeneous incorporation of lignin into the polystyrene thermoplastic matrix.

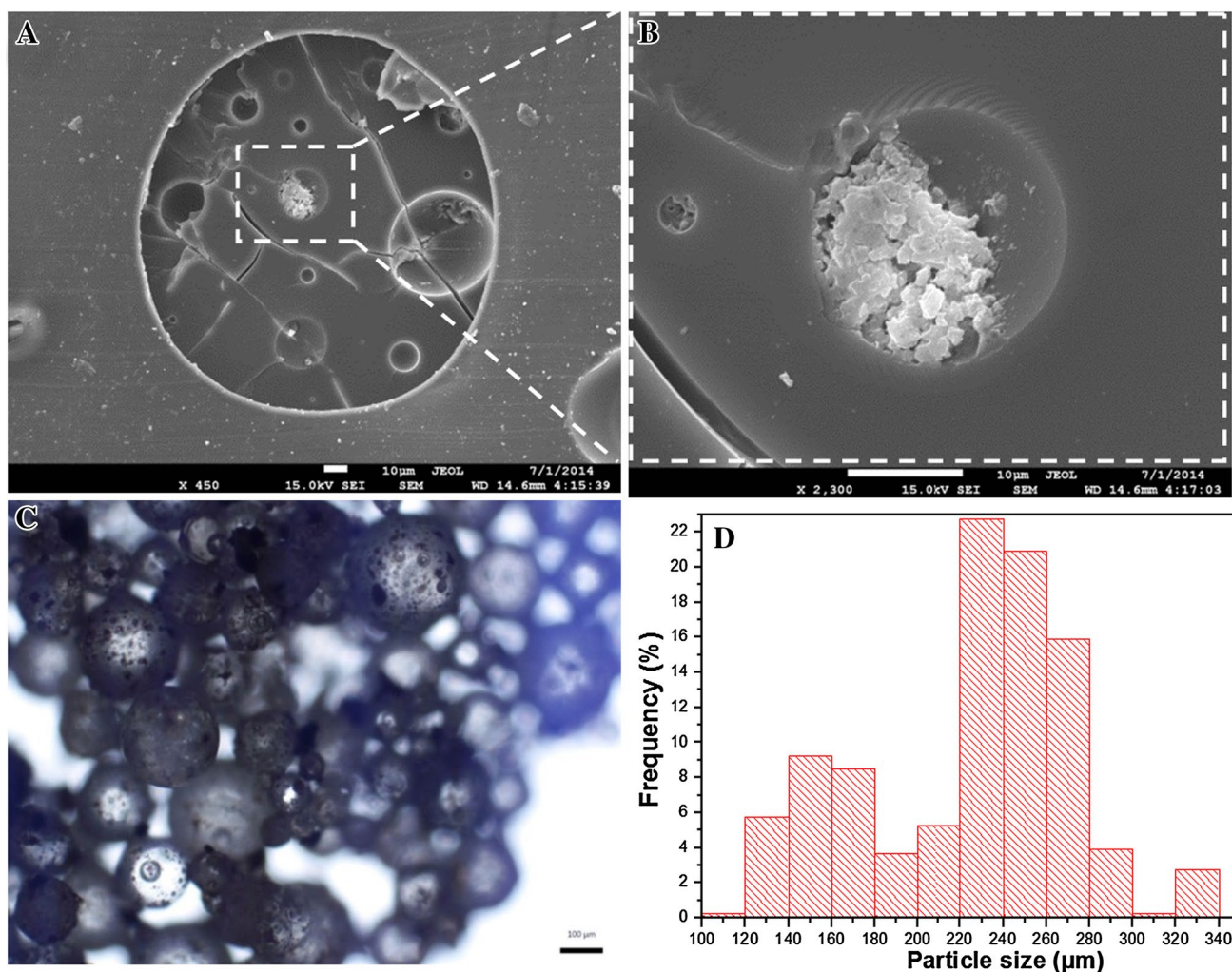
For reactions pertaining to 20% lignin, 10 g/L PVA was used. The higher concentration gave a better effectiveness for the suspending agent (PVA), based on the stability of the reaction medium. The increased mass of the polymerization initiator to 9.05 g (11.5 wt%), was necessary to compensate for the increase in the lignin fraction of the reaction medium, due to their susceptibility to oxidation by the polymerization initiator, which ultimately leads to reduction in monomer conversion. Based on the yield of the reaction, which was equivalent to 98.8%, it is reasonable to assume that the concentration of BPO used was sufficient to ensure proper supply of initiator radicals during the reaction.

### Mass-Suspension Polymerization with Styrene and Esterified Lignin

The polymer composites were also formed from esterified lignin presenting an average size between 75 and 100  $\mu\text{m}$  and styrene. The polymerization reactions were carried out following the same experimental protocol employed to produce composites with natural lignin, where the first step was maintained under stirring conditions at 1000 rpm, followed by the second stage, consisting of the addition of PVA solution under constant agitation speed of 500 rpm. Table 4 exhibits the experimental conditions of the reactions with 5, 10 and 20% of esterified lignin and their respective conversions.

**Table 3** Experimental conditions of the sequential mass-suspension polymerization processes using natural lignin

Experiment	Lignin (%)	Styrene (g)	Lignin (g)	PVA (g/L)	BPO (g)	Conversion (%)
1	0	58.1	0	5	2.04	95.8
2	0	58.1	0	7	4.08	96.7
3	0	58.2	0	10	9.04	98.6
4	5	58.2	2.1	5	2.08	93.1
5	5	58.1	3.0	5	2.06	96.1
6	5	58.3	2.9	5	2.04	97.3
7	5	58.1	2.9	5	2.05	97.7
8	10	58.1	5.8	5	2.05	78.3
9	10	58.3	5.9	5	4.07	84.3
10	10	58.0	5.9	7	4.07	97.8
11	20	58.1	11.7	10	9.05	98.8



**Fig. 8** Characterization of polymer composite obtained with natural 5 wt% natural lignin, regarding to Experiment 6 with conversion of 97.3%. SEM micrograph (a and b), light microscopy (c) and particle size distribution (d)

Experiment 12 corresponds to the polymer composite obtained through classical suspension polymerization reaction performed with 5% of esterified lignin and 5 g/L of suspending agent (PVA) with yield of 93.7%. According to Fig. 10, there is a low incorporation of the lignin into the polymer matrix, cluster of lignin particles on the surface of the polymer and free lignin structures without incorporation. It is also possible to observe lignin particulates inside macrocavities of the polymer particles. This result shows that the partial modification of the lignin cannot guarantee that it will be fully distributed homogeneously in the thermoplastic matrix of polystyrene.

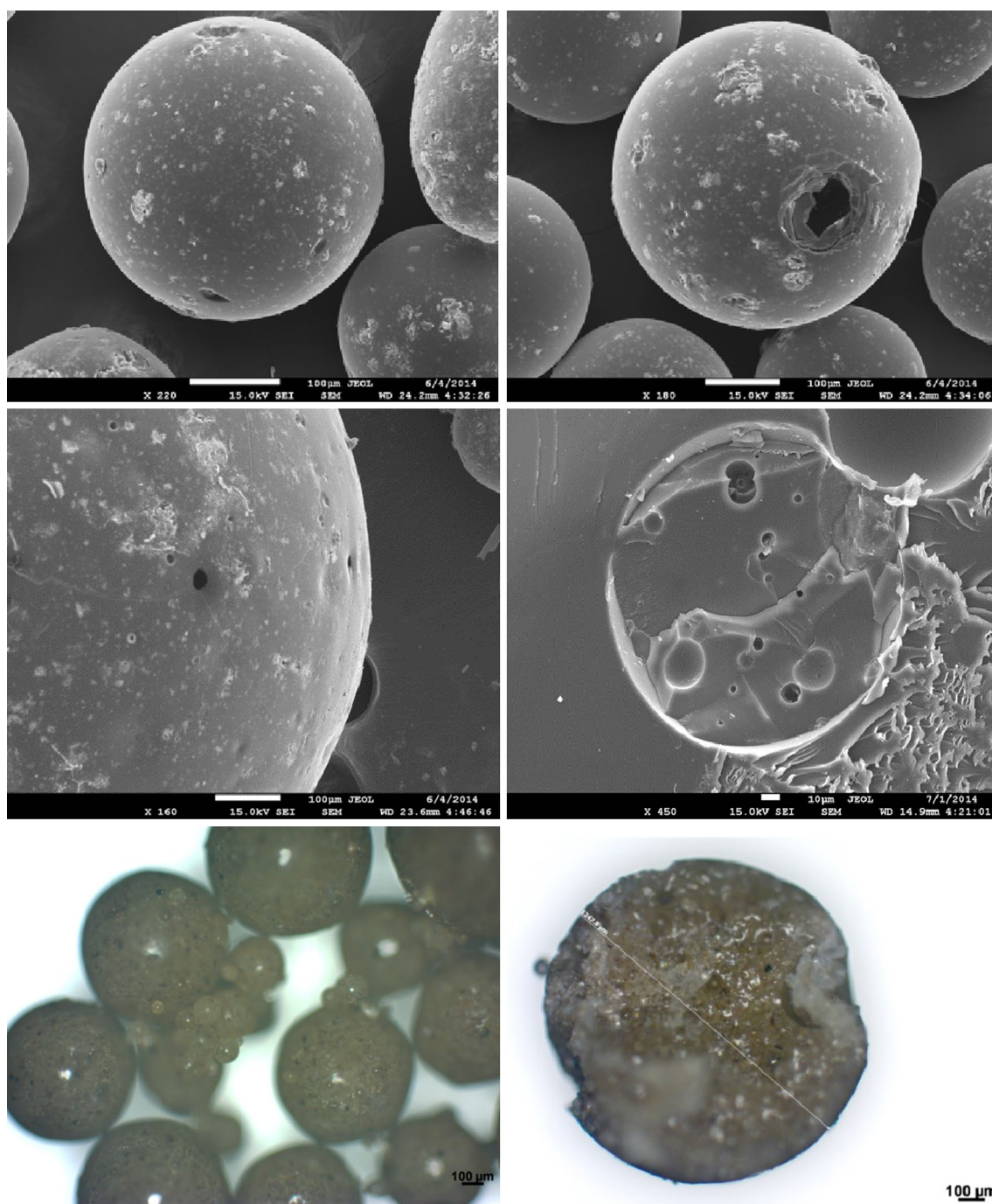
As an attempt to minimize the segregation of lignin particles, for practical reasons, reactions with esterified lignin were also carried out via sequential mass-suspension polymerization. Experiment 13 is related to the polymer composite synthesized with 5% of esterified lignin, 10 g/L of suspending agent and 2.04 g (3.2 wt%) of initiator of

polymerization, demonstrated a conversion of 98.8%. Although the polymers formed were not of spherical shape due to the low stirring speed, presenting a porous structure, the reaction medium was kept stable during the reaction course, as shown in Fig. 11. Furthermore, the incorporation of lignin is observable.

In regards to the reaction containing 10% esterified lignin (Experiment 14, Fig. 12) with conversion around 98.7%, the suspending agent solution was increased to 30 g/L in order to enhance stability. The polymers formed expressed a good morphology (as a result of the stability of the reaction medium) and high porosity (as a consequence of the migration of water microdroplets, encapsulated in the polymeric matrix, to the reaction medium).

DSC measurements revealed that the incorporation of esterified lignin increased the glass transition temperature of the polymer composites [e.g.  $T_g = 97^\circ\text{C}$ , formed with BPO 2.04 g ( $\approx 3.2$  wt%) and lignin 5%] in comparison to





**Fig. 9** SEM image of polymer composites with 10 wt% natural lignin, regarding to Experiment 10 with conversion of 97.8%

both the polystyrene homopolymer [e.g.  $T_g = 91^\circ\text{C}$ , formed with BPO 2.04 g ( $\approx 3.2$  wt%)] and the composite presenting natural lignin (e.g.  $T_g = 91^\circ\text{C}$ , formed with BPO 2.04 g and lignin 5%).

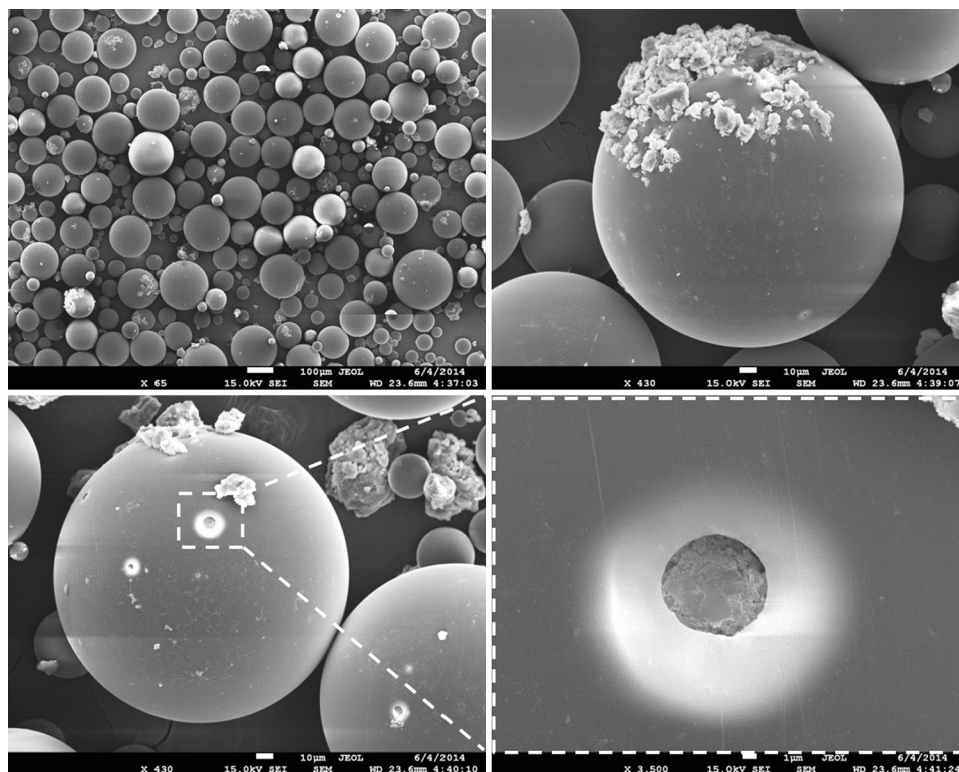
Experiment 15 corresponds to the polymer composite synthesized with 20% esterified lignin, 30 g/L of PVA aqueous phase and 4.07 (6.0 wt%) of benzoyl peroxide. This reaction exhibited low conversion around 83.1%

due to the low amount of initiator of polymerization and instability of the reaction mixture due to the low concentration of the suspending agent. These problems are easily overcome when polymer reactions are carried out with 20% esterified lignin, a suspending agent solution of 50 g/L and 9.01 (11.4 wt%) of BPO. Experiment 16 can be regarded as a representative example, where polymer

**Table 4** Experimental conditions of the sequential polymerization mass-suspension processes using esterified lignin

Experiment	Esterified lignin (%)	Styrene (g)	Esterified lignin (g)	PVA (g/L)	BPO (g)	Conversion (%)
12 <sup>a</sup>	5	58.05	2.90	5	2.04	93.7
13	5	58.10	2.94	10	2.04	98.8
14	10	58.08	5.88	30	4.07	98.7
15	20	58.03	11.60	30	4.07	83.1
16	20	58.12	11.60	50	9.01	99.1

<sup>a</sup>Polymer composite formed through classical suspension polymerization process

**Fig. 10** SEM image of Experiment 12, correspondent to the polymer composite obtained from 5 wt% esterified lignin and conversion of 93.7% via classical suspension polymerization process

composites presenting conversion of 99.1% was formed with good morphology and porous structure.

As a matter of the fact that the amount of initiator used in suspension polymerization reactions generally lying in the range 0.1 to 0.5% related to the monomer(s) [28, 40]. For the reactions with both the natural lignin and esterified lignin this value was 3.5%, almost seven times higher. This high amount of BPO was necessary due to the ability of lignin to undergo oxidation reaction [41–47]. The higher the lignin concentration, the higher the benzoyl peroxide amount, in order to ensure the growth of the polymer chains and compensate the fraction of initiator radicals that acts as an oxidizing agent.

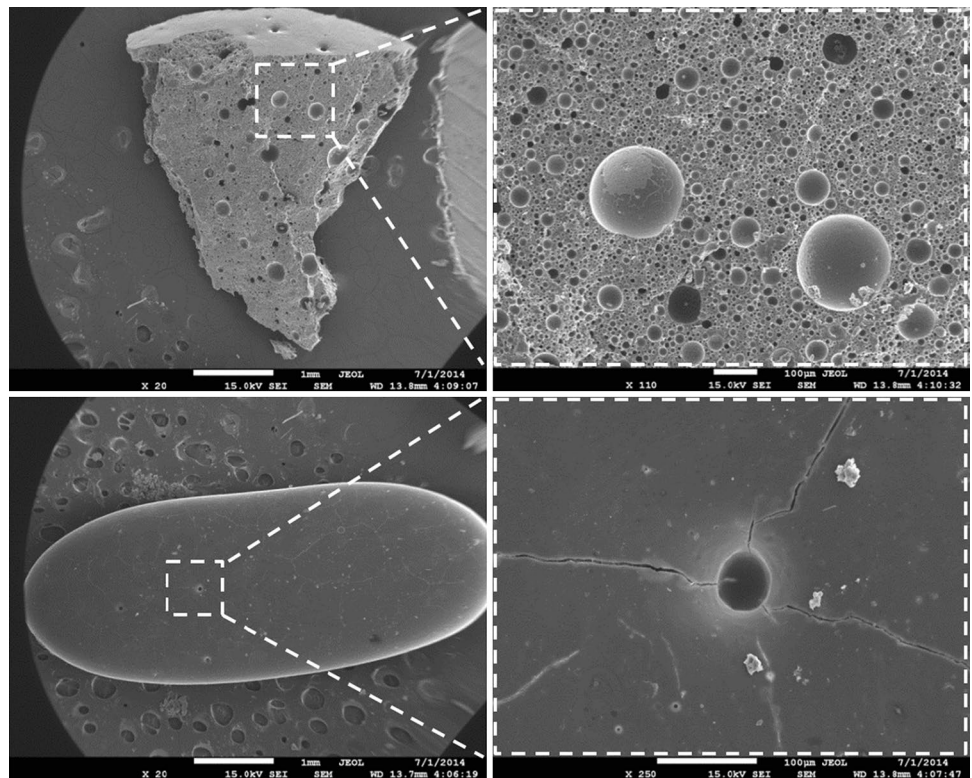
It is also well-known that the combined action of suspending agent and mechanical stirring affects significantly the shape of polymer particle, average particle size and the distribution of particle size. The PVA solution plays

an important role on the stability of the reaction medium, reducing the interfacial tension between the water and the organic phase and protecting (N.B. PVA molecules adsorbed on the surface of the monomer droplets produces a thin layer, which prevents coalescence of the monomer droplets) the monomer droplets formed due to the application of high shear rates through mechanical stirring [48].

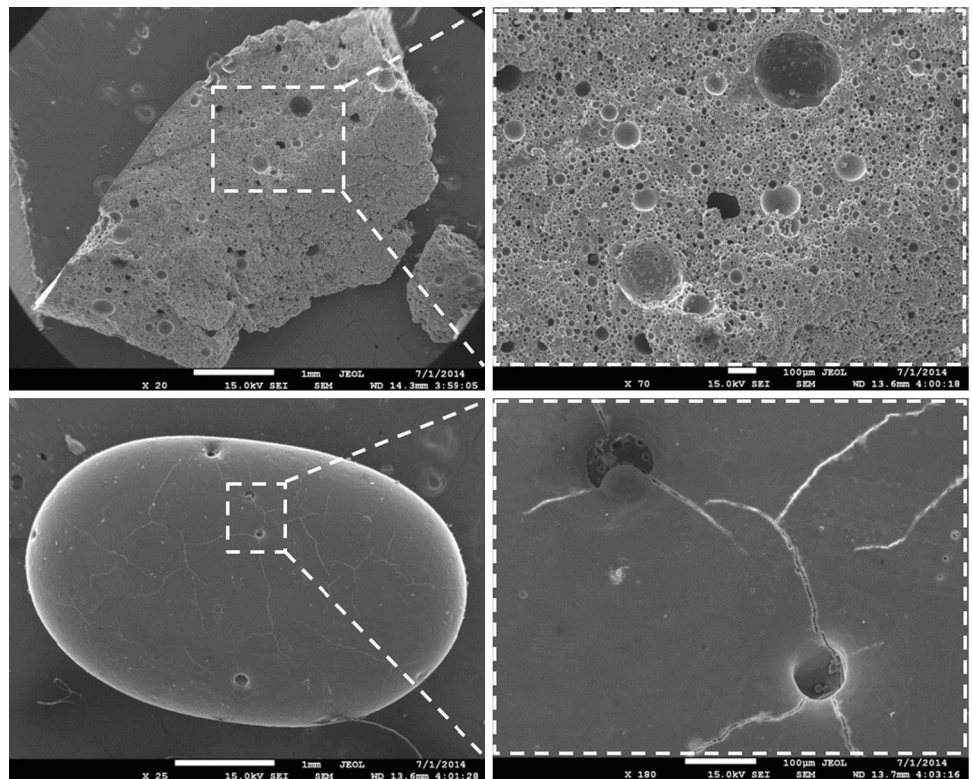
As previously discussed, the lignin added to reactor seemed to contribute to the instability of the polymerization medium requiring large concentration of PVA. To evaluate the acidity of the reaction medium after addition of water pH measurements were performed, as shown in Table 5 [49]. It is observed that the acidity of the reaction medium increases as the lignin amount is also increased, which explains the high concentration of PVA needed to stabilize the monomer droplets during the polymerization reaction.



**Fig. 11** SEM image of the obtained polymers synthesized with 5 wt% esterified lignin, regarding to Experiment 13 with conversion of 98.8%



**Fig. 12** SEM image of the obtained polymers synthesized with 10 wt% esterified lignin, regarding to Experiment 14 with conversion of 98.7%



A preliminary viscosity study was performed with the following polymer samples: pure polystyrene and polymeric composites containing 5 wt% of natural or esterified

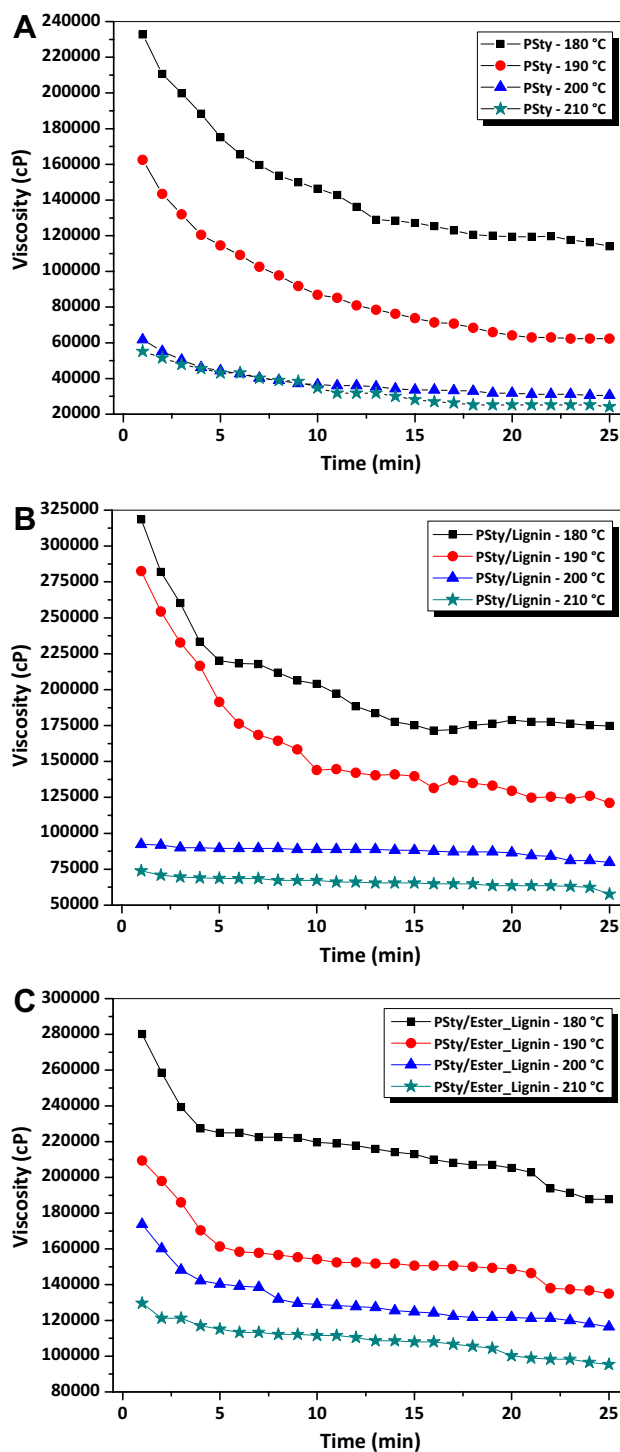
lignin. Viscosity assays were carried out at four different temperatures (180, 190, 200 and 210 °C) with a stirring speed of 0.1 rpm and a shear rate of 0.03 s<sup>-1</sup>. Viscosity

**Table 5** pH measurements of aqueous phase containing natural and esterified lignins

Lignin (%)	Water (mL)	Natural lignin		Esterified lignin	
		Mass (g)	pH	Mass (g)	pH
0	3	0.0000	5.52	0.0000	5.52
5	3	0.0673	2.55	0.0652	2.67
10	3	0.1303	2.32	0.1299	2.54
20	3	0.2589	2.10	0.2598	2.46

profiles portrayed in Fig. 13 indicate that in comparison to pure polystyrene (PSty), the viscosity of both the polystyrene/lignin (PSty/Lignin) and the polystyrene/esterified lignin (PSty/Ester\_Lignin) was significantly affected by the presence of lignin, exhibiting an increase of approximately 1.5 to 3.9 times, depending on the analysis condition and lignin type (natural or modified), as illustrated in Table 6. The thermal stability of the polymers was slightly increased when 5 wt% of lignin was incorporated to the thermoplastic matrix of polystyrene (see Fig. 14). The glass transition temperature ( $T_g$ ) of samples submitted to viscosity essays determined through DSC measurements was kept unchanged, which means that viscosity essay temperature (in the range from 180 to 210 °C) does not contribute to the degradation of the polymeric chains, which is expected to take place at temperatures values above 300 °C, as showed in Fig. 14. Polymers exhibited good stability to the processing temperature and only a significant weight loss (320–460 °C) and thermal degradation similar to the pure polystyrene.

It is well-known that in mass and suspension polymerization process the amount of initiator plays a fundamental role on the average molar masses of the polymer and can be properly manipulated to tailor the growing polymer chains. As depicted in Fig. 15 and Table 7, the higher the initiator concentration, the lower the average molar masses of the final polymer. The observed effect of BPO on the average molar masses is in agreement with the findings of other investigators reported elsewhere [50]. In general, styrene/lignin-based polymers exhibited higher average molecular masses in comparison to the values observed for polystyrene homopolymer when similar amounts of BPO are considered, which reflects the ability of lignin to quench the radical polymerization, as the lignin molecules are oxidized by a fraction of BPO initiator radicals, allowing the effective growth of the polymeric chains. In particular for styrene/esterified lignin-based polymer, it



**Fig. 13** Viscosity profiles of the polystyrene homopolymer (a), styrene/natural lignin-based polymer (b) and styrene/esterified lignin-based polymer (c). (N. B. Styrene/lignin-based composites containing a lignin fraction of 5 wt%.)

**Table 6** Thermal characterization of polystyrene homopolymer and styrene/lignin-based polymers synthesized with a lignin fraction of 5 wt%

Sample	Viscosity ESSAY (°C)	Viscosity (cP)	$T_g$ (°C)	Conversion (%)
Polystyrene	–	–	94.50	96.9
	180	113,976	94.21	
	190	62,387	94.95	
	200	30,594	94.45	
	210	24,194	93.74	
Polystyrene/natural lignin	–	–	85.55	97.3
	180	174,653	88.90	
	190	121,174	87.43	
	200	79,783	89.31	
	210	57,588	87.48	
Polystyrene/esterified lignin	–	–	94.48	86.3
	180	187,760	91.87	
	190	134,971	91.66	
	200	116,375	93.09	
	210	95,380	93.26	

seems that the functionalized lignin is more sensitive to the presence of initiator radicals, acting more effectively as a free-radical scavenger, which lead to formation of polymer with high molar masses within the range of the experimental conditions adopted here.

Figure 16 shows the correlations between number-average molar mass ( $M_n$ ) and viscosity obtained in different temperatures for polystyrene homopolymer and styrene/lignin-based polymeric materials synthesized with 5 wt% of lignin (natural and esterified). It is observed that the dynamic viscosity data are linearly correlated to the  $M_n$  values, exhibiting correlation coefficients ( $R^2$ ) lying in the interval from 0.95 to 1.00.

## Conclusions

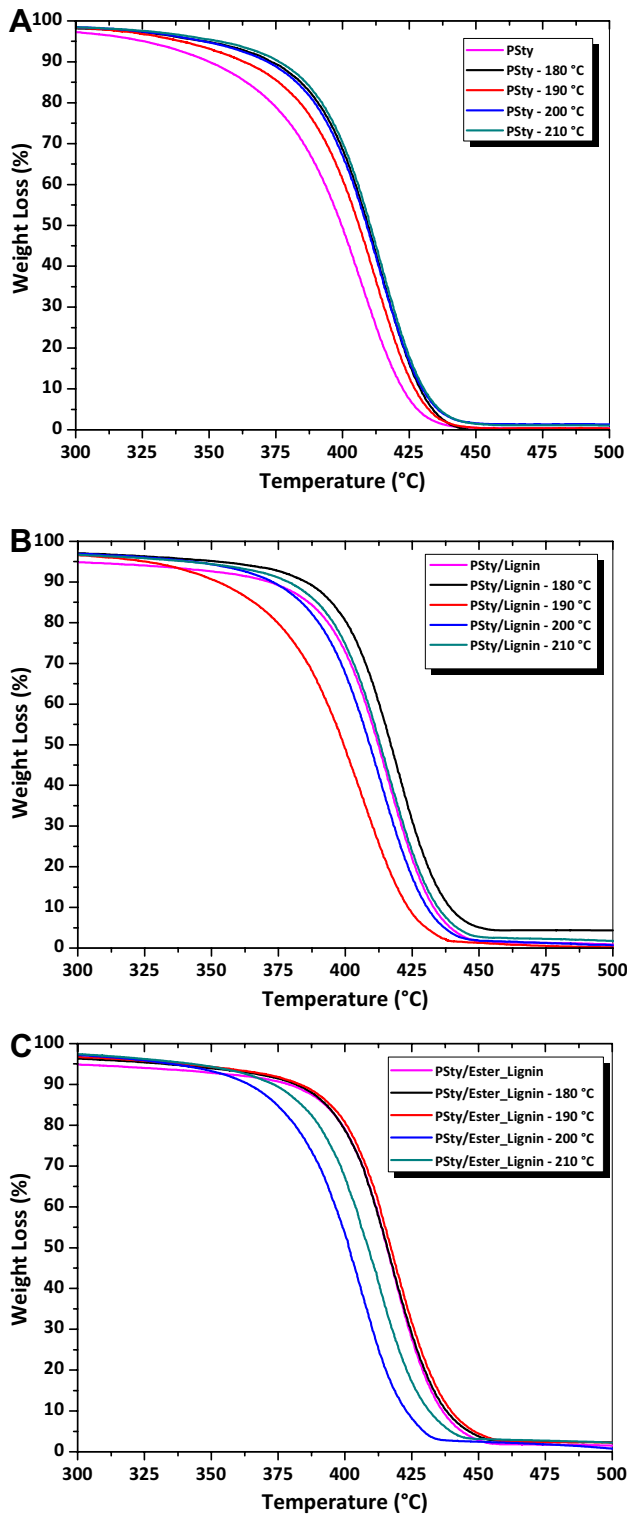
In this work, both natural and esterified lignin were incorporated into the polystyrene matrix with the purpose of forming polymeric composite material. Firstly, a modified lignin employed as extraction method provided lignin samples with a yield of approximately 50%. The subsequent esterification with methacrylic anhydride lignin had a yield of approximately 64%. Both the esterification and the extraction of lignin were proven by infrared (IR) and NMR  $^1H$ , showing the typical peaks and also demonstrating a good substitution of the hydroxyls present in lignin. The thermal behavior was analyzed by TGA and DSC characteristic curves, which showed that the natural lignin and improved thermal stability of the esterified lignin.

The sequential mass-suspension polymerization process was adequate because it provided a better homogeneity of the organic phase of the reaction medium, formed

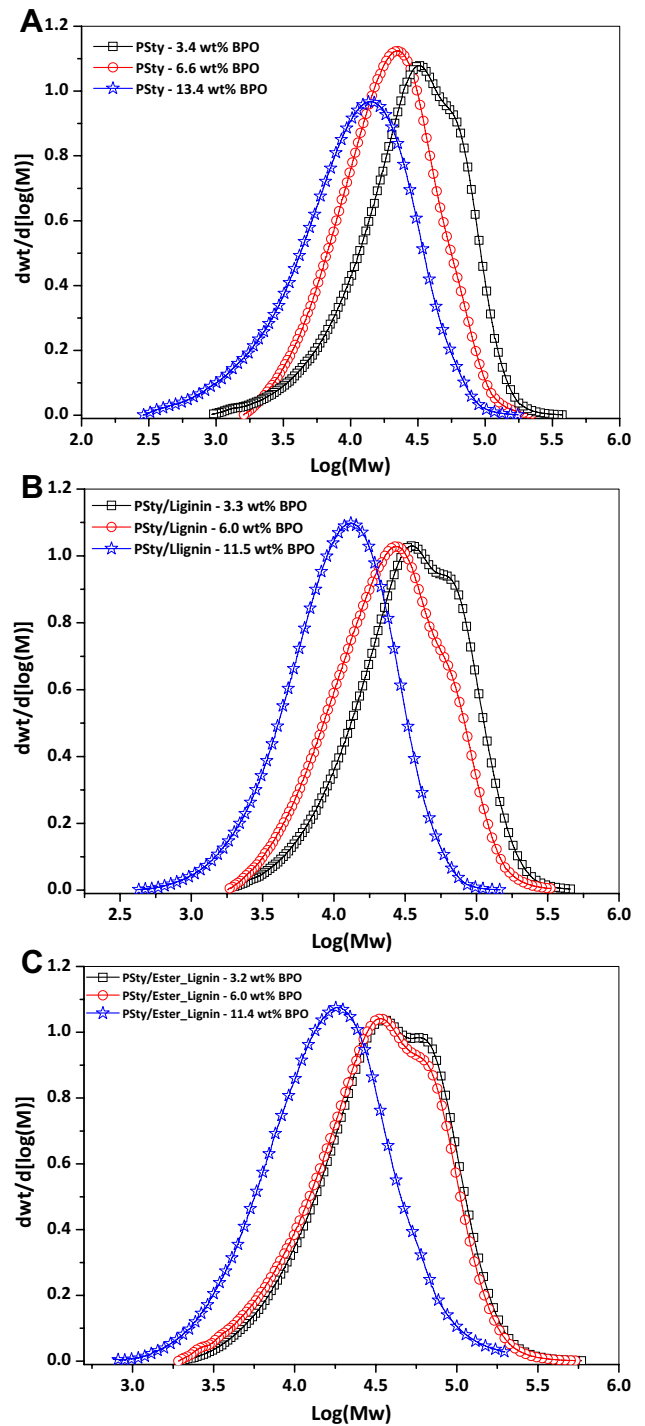
homogeneous polymers, and ensured adequate dispersion of the components during the reaction. The composite formed by the combination of natural lignin and styrene was successfully obtained. Their spherical morphology was confirmed by SEM and light microscopy; both also showed that the lignin was incorporated in the polymer and that the particles formed possess macro cavities.

The polymeric composite formed by the combination of esterified lignin and styrene showed no spherical morphology and high porosity. Due to the porous structure this polymer composite may be used as support and adsorbent material. In particular, with regards to the analytical area, porous polymers may be used as stationary phase in chromatography or as support for catalysts. Viscosity of the lignin-based polymeric composites significantly increased when compared to the pure polystyrene as a result of the presence of lignin. Depending on the temperature of the viscosity tests and the lignin type (natural or modified), the viscosity of polymer composites increased approximately 1.5 to 3.9 times. The average molar masses of the polymers were significantly affected for both the amount of initiator and type of lignin. In summary, the molar masses decreased as BPO concentration was increased and the styrene/lignin-based polymers exhibited the highest molar masses, as a result of the high capacity of the lignin to scavenger free-radical of initiator.

It is very important to highlight that based on a very simple polymerization system, it is possible to control the morphology of composite materials and additionally to enhance the final properties of polystyrene polymers through the incorporation of lignin, which represents a potential platform for the development of attractive polymeric materials based on renewable resources.



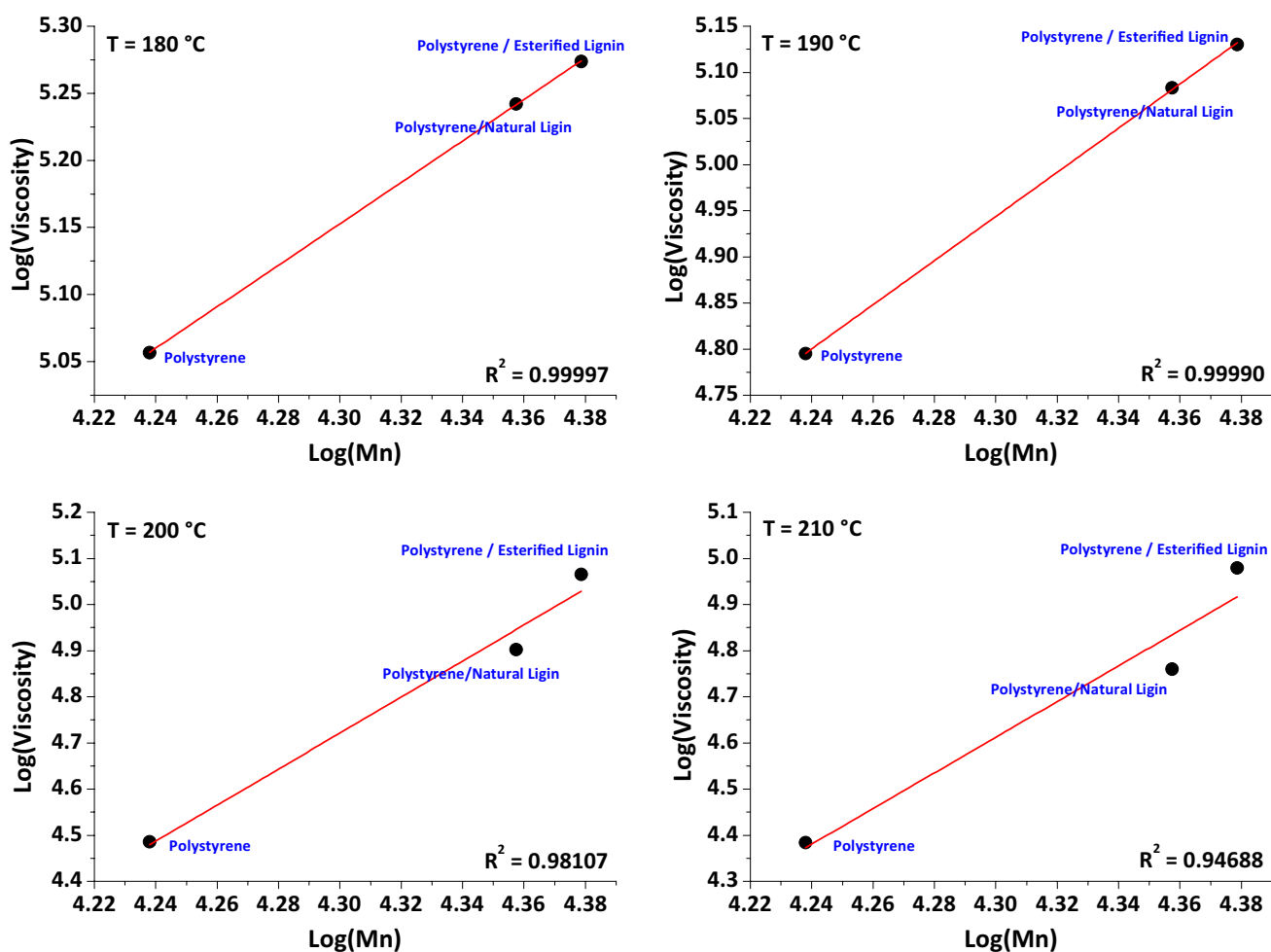
**Fig. 14** Thermal stability of polystyrene homopolymer (a), styrene/natural lignin-based polymer (b) and styrene/esterified lignin-based polymer (c). (N. B. Styrene/lignin-based composites containing a lignin fraction of 5 wt%.)



**Fig. 15** Molar mass distribution of styrene/lignin-based polymeric materials: **a** Polystyrene homopolymer, corresponding to the Experiments 1 to 3 in Table 7 **b** Styrene/natural lignin, corresponding to the Experiments 7, 10 and 11 in Table 7, and **c** styrene/esterified lignin composites, corresponding to the Experiments 13, 14 and 16 in Table 7

**Table 7** Number-average molar mass ( $M_n$ ), mass-average molar mass ( $M_w$ ) and molar-mass dispersity ( $D_M$ ) of styrene/lignin-based polymeric materials: Polystyrene homopolymer, Styrene/natural lignin and styrene/esterified lignin composites

Sample	Experiment	Styrene (g)	Lignin (g)	BPO (%)	$M_n$ (g/mol)	$M_w$ (g/mol)	$D_M$
Polystyrene	1	58.06	0.00	3.4	17,300	38,900	2.25
	2	58.10	0.00	6.6	13,200	25,400	1.92
	3	58.19	0.00	13.4	5700	15,600	2.74
Polystyrene/natural lignin	7	58.10	2.90	3.3	22,800	48,700	2.14
	10	58.00	5.90	6.0	16,300	34,800	2.13
	11	58.10	11.70	11.5	7200	14,700	2.04
Polystyrene/esterified lignin	13	58.10	2.94	3.2	23,900	49,200	2.06
	14	58.08	5.88	6.0	21,300	45,400	2.13
	16	58.12	11.60	11.4	10,700	23,000	2.15

**Fig. 16** Correlation between number-average molar mass ( $M_n$ ) and viscosity data for styrene/lignin-based polymeric materials synthesized with a lignin fraction of 5 wt%

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