Preparation and Characterization of Lignin Polymeric Nanoparticles Using the Green Solvent Ethylene Glycol: Acid Precipitation Technology

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Alkali lignin (AL) was prepared by the acidification of black liquor obtained from a pulp and paper factory. The average molecular weight of the AL (2,530 g/mol) was determined using gel permeation chromatography (GPC). Alkali lignin modified by ethylene glycol and lignin nanoparticles (LN) were prepared *via* acid precipitation technology. Reactions in a pH range of 4 to 6 were evaluated while preparing the nanoparticles. Lignin nanoparticles were stable at pH 4 to 10. The sizes of the nanoparticles were assessed with dynamic light scattering (DLS); the average diameter of the nanoparticles at pH 4 was 52.7 nm, which was confirmed by SEM. LN has polar centers that can produce an interacting interface with the polymer matrix in which it will be dispersed. The morphologies and structures of combinations of AL and LN were investigated using scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FT-IR), and thermogravimetric analysis-derivative thermogravimetric (TGA-DTG). The FTIR spectra clearly showed that the positions of the peaks in lignin nanoparticles shifted to slightly lower values due to the interaction between lignin molecules and ethylene glycol.

Keywords: Alkali lignin; Biomaterial; Polymer; Nanoparticles; Ethylene glycol

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INTRODUCTION

After cellulose, lignin is the second most abundant natural polymer. It consists of phenylpropane structural units with carbon-carbon and ether connections. Lignin is a complex amorphous structure that has yet to be fully investigated (Guo *et al.* 2017). Because lignin constitutes 15 to 36% of wood by weight, lignin sources are abundant and suitable for use in the wood and paper industries (Gellerstedt 2015). Alkali lignin (AL), cellulose, and hemicellulose have characteristics that are suitable for adsorption and ion exchange. However, chemical modification of lignin from natural material is required.

All the properties that occur in nanoparticles can be explained by two factors: increasing the surface relative to the volume and discontinuing the energy levels. In general, by changing the size of nanoparticles in the range from 1 to 100 nm, the surface-to-volume ratio and the distance between energy levels changes. These two variables cause many changes in properties and features. In other words, by controlling the size of nanoparticles, can control their properties, which is very important.

Nanoparticles prepared from natural biomaterials could potentially be harmless for humans, as well as benign for the environment. There is wide range of applications for the preparation of such environmentally biodegradable nanoparticles from renewable natural materials, such as cellulose, hemicellulose, lignin, chitosan, and other naturally occurring and abundant biopolymers (David *et al.* 2014). At present, there is a vast number of reports of successful synthesis routes for cellulose nanoparticles (Moon *et al.* 2011). Lignin is one of the major components of plant cell walls and it is extracted mainly from timber during the production of paper, but it can also be extracted from other plant sources or bio-mass by-products and waste (Fakhrullin *et al.* 2012).

Polymer nanotechnology has been efficiently utilised in the delivery of drugs, oligonucleotides, and RNA interfering effectors. However, preparation of nanoparticles from polymers has become an important challenging component of this technology (Vauthier and Bouchemal 2009). Fabrication of nanoparticles from natural polymeric materials such as lignin gained prominence due to its environmental compatibility. Lignin is available in abundance as a waste material from the pulp and paper industry. Yet, its utilisation as nanoparticles is mostly limited and/or associated with patents (Yeo *et al.* 2015).

The studies of Frangville *et al.* (2012) have shown that nanoparticles synthesised from low sulphonated lignin were non-toxic towards microalgae and yeast. Thus, utilisation of lignin in various industrial formulations and consumer products such as sunscreens and paints would play an important role in reducing their potential hazardous risks on mankind. Nanoscale lignin prepared by supercritical antisolvent process was shown to possess enhanced antioxidant activity when compared to non-nanoscale lignin, due to their high surface-area-to-volume ratio with reference to their parent polymers (Lu *et al.* 2012). AL, which is produced from the paper and pulp industry by kraft pulping process, was chosen for comparative analysis, due to its usage in many industrial applications.

Srinivasa and Kollipara (2016) have shown that dioxane lignin (DL) and AL nanoparticles can be synthesised from acetone and water (9:1, v/v). Both DLNP and ALNP were fabricated in spherical shape with mean size of 80 to 104 nm.

Successful utilization of lignin nanoparticles that can reinforce phenolic foams, stabilize Pickering emulsions, and carry silver ions or silver nanoparticles has been reported in the literature (Del Saz-Orozco *et al.* 2012; Wei *et al.* 2012; Yi *et al.* 2015; Nypelö *et al.* 2015; Richter *et al.* 2015). Furthermore, as water-dispersed polymer nanoparticles have been widely investigated in drug delivery systems (Langer 1998), lignin nanoparticles could be a potential precursor for drug delivery applications.

Despite the obvious need for well-defined aqueous lignin nanoparticle dispersions, only a few scientific articles on lignin-based nanoparticles have been published. Frangville *et al.* (2012) were among the first ones to report on aqueous lignin nano-particle dispersions. They produced nanosized lignin particles through dialysis by using ethylene glycol as a solvent (Yiamsawas *et al.* 2014). However, the obtained particles were rather irregular in size and shape. Qian *et al.* (2014a) prepared spherical nanoparticles from acetylated lignin using tetrahydrofuran (THF) as a solvent and induced the particle formation by dropwise addition of water to the lignin solution (Gilca *et al.* 2015). Yiamsawas *et al*. (2014) introduced lignin-based nanocapsules which may have potential in agricultural applications (Gonugunta *et al.* 2012), and Gilca *et al*. (2015) modified lignin with ultra-sonication in order to produce nanoparticles (Qian *et al.* 2014a). Gonugunta *et al*. (2012) produced lignin based carbon nanoparticles by freeze-drying a lignin solution followed by a thermal carbonization process (Miikka *et al.* 2015). Moreover, Qian *et al.* (2014a) proposed a novel method for using CO_2 and N_2 gas responsive lignin based nanoparticles as a surfactant for Pickering emulsions.

The lignin nanoparticle preparation methods reported so far have major limitations considering potential industrial processes. Qian *et al.* (2014b) used acetylated lignin. This step required environmentally hazardous chemicals such as acetyl bromide. Additionally, in order to get high concentrated nanoparticle dispersions, a significant amount of water would need to be evaporated, which consumes energy. Furthermore, in the methods described by Yiamsawas *et al.* (2014), Frangville *et al.* (2012), and Gilca *et al.* (2015), the final lignin nanoparticles had irregular shapes. This may lead to application challenges if spherical particles are desired. Moreover, hazardous chemicals were utilized in these particle preparation methods including toluene diiso-cyanate by Yiamsawas *et al.* (2014), and pyridine by Qian *et al.* (2014b).

Miikka *et al.* (2015) introduced a straightforward method to produce lignin nanoparticles from waste lignin obtained from kraft pulping. Spherical lignin nanoparticles were obtained by dissolving softwood kraft lignin in tetrahydrofuran (THF) and subsequently introducing water into the system through dialysis. No chemical modification of lignin was needed. Water acts as a non-solvent reducing lignin's degrees of freedom causing the segregation of hydrophobic regions to compartments within the forming nanoparticles (Miikka *et al.* 2015).

Currently, societal regulations and environmental consequences have raised several implications for the need for developing alternate carbon nanomaterials for petroleum based resources. Lignin has been found to be efficient precursors for the synthesis of carbon nanostructures due to its high carbon rich chemical structure and easy accessibility to chemical modification. Syntheses of carbon nanostructure from lignin have not been explored extensively.

The purpose of this research was to prepare lignin nanoparticles (LN) using acid precipitation technology, which is environmentally friendly. For this purpose, ethylene glycol was used as the solvent. The size of lignin nanoparticles was determined. To identify the characteristics of LN, their structural changes, surface morphology, and thermal behavior were examined.

EXPERIMENTAL

Materials

Alkali lignin was prepared by the acidification of black liquor obtained from the Khuzestan Pars paper factory in Iran. The characteristics of the black liquor are presented in Table 1. Sodium hydroxide (99%), hydrochloric acid (36 wt.%), and ethylene glycol (98%) were purchased from Merck (Darmstadt, Germany). Ethanol (99.9%) was supplied by Bidestan (Qazvin, Iran).

Table 1. Black Liquor Compounds in Bagasse Soda Cooking (%)

Lignin	Holo cellulose	Ash	Na	O	S	H	C	Other ions
25.6	32.4	42	14.8	34	0.3	4.5	44.8	1.6

Fourier transform infrared spectroscopy (FT-IR) was used to determine the chemical structures of the compounds in the range of 400 to 4,000 cm^{-1} using a Tensor 27 FT-IR spectrophotometer (Bruker, Ettlingen, Germany). The pH was determined using a Model Metrohom 827 pH meter (Metrohm, Herisau, Switzerland). A thermogravimetric analysis-derivative thermogravimetric (TGA-DTG) device (N5370210, Perkin Elmer, Massachusetts, USA) was used to study structural changes in the synthesis of compounds as well as heat resistance up to 500 °C. A Zetasizer PSS0012-22 (Malvern, Pennsylvania, USA) was used for dynamic light scattering (DLS). Scanning electron microscopy (SEM) (Model LEO 1455VP, Labx, London, UK) was used to determine the particle size and surface morphology. Gel permeation chromatography (GPC) was performed with a Shimadzu 6-A (Tokyo, Japan) to determine the molecular weight of the AL.

Methods

Preparation of alkali lignin

To precipitate the AL, acidic black liquor from a pulp and paper factory in Khuzestan was placed in 0.1 N hydrochloric acid in a pH range of 2.5 to 3. The impure lignin precipitate sediment was centrifuged and isolated. The sediment was washed with distilled water until the filter effluent reached a pH of about 7. Lignin was dissolved in warm ethanol (50 to 60 °C). Ethanol-soluble fractions were separated by filtration, and the solid residue was discarded. The bulk of the ethanol (75%) in the evaporator was evaporated at low pressure. Distilled water was poured on the remaining solution and the sediment of lignin in a colloidal form. After centrifugation for 10 min at 4,500 rpm at room temperature, a considerable amount of purified lignin was obtained (Mirshokraie 2011). The molecular weight and polydispersity index of the AL obtained using gel permeation chromatography are presented in Table 2.

Table 2. Molecular Weight of Alkali Lignin

Polydispersity Index (PDI)	Number Average Molecular Weight (M_n)	Weight Average Molecular Weight (M_w)	Compound
1.65	1528	2530	AL

Preparation of lignin nanoparticles

Alkali lignin (0.28 g) was dissolved in 50 mL of polyethylene glycol (0.56 wt.%) and stirred for 2 h at 40 °C. It was filtered with 0.4-μm filters for purification. Next, 0.25 M hydrochloric acid was slowly dropped into 45 mL of the filtered solution at pH 4. The nanoparticles were formed in this solution. After centrifugation, the nanoparticles were washed with distilled water and dried under vacuum at 50 °C (Gupta *et al.* 2014).

RESULTS AND DISCUSSION

Determining Lignin Nanoparticle Size Using Dynamic Light Scattering

The particle size distribution of lignin nanoparticles at pH 4, as a function of the percentage of nanoparticles, is presented in Fig. 1. The AL nanoparticle size at pH 4 was between 40 nm and 60 nm and the average diameter of the nanoparticles was 52.7 nm. The average diameter of the AL nanoparticles produced by nitric acid and pH reductions recently was estimated to be 278 nm (Krachler *et al.* 2012).

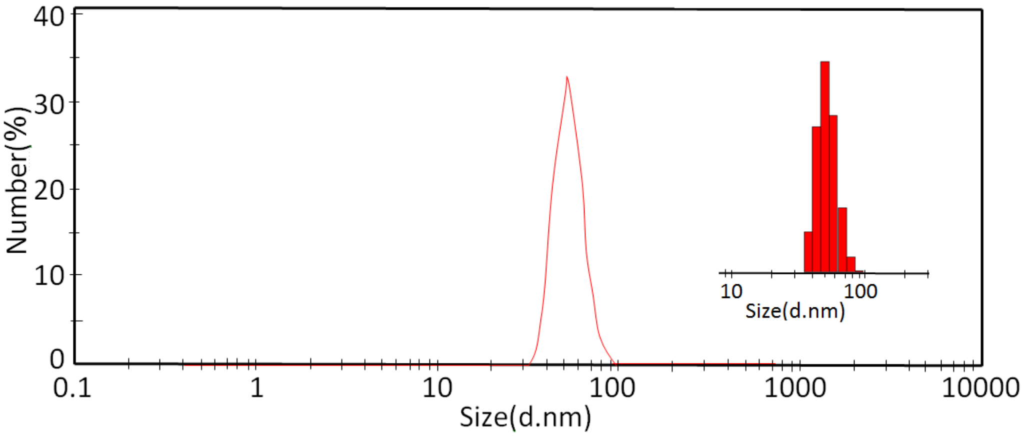

Fig. 1. Particle size distribution of lignin nanoparticles

Effect of pH on the Size of Lignin Nanoparticles

Figure 2 shows the effect of the pH during synthesis on the minimum, maximum, and average diameters the AL nanoparticles. The LN produced between pH 4 and 6 were of appropriate diameter. The smallest nanoparticles were synthesized at pH 4. The average nanoparticle diameters at pH 4, 4.5, 5, 5.5, and 6 were 52.7 nm, 53.9 nm, 56.3 nm, 59.5 nm, and 62.4 nm, respectively.

Considering that the pK_a for the protonation of alcoholic groups in lignin is about minus 2 (K_a = 10^2), alcoholic groups have high acidity and protonate at low pH. By decreasing the pH and increasing the concentration of H^+ ions, the number of alcoholic cations increases. Finally, lignin nanoparticles form. Logic would suggest that lowering the pH causes coagulation and agglomeration of soft, oil-loving particles in the lignin. Because the pK_a of phenoxy groups is about 10.2, lignin are stable between pH 4 to 6. Similarly, at pH's greater than 10, phenoxy groups are created and the lignin will dissolve in alkaline environments (Frangville *et al.* 2012; Gupta *et al.* 2014).

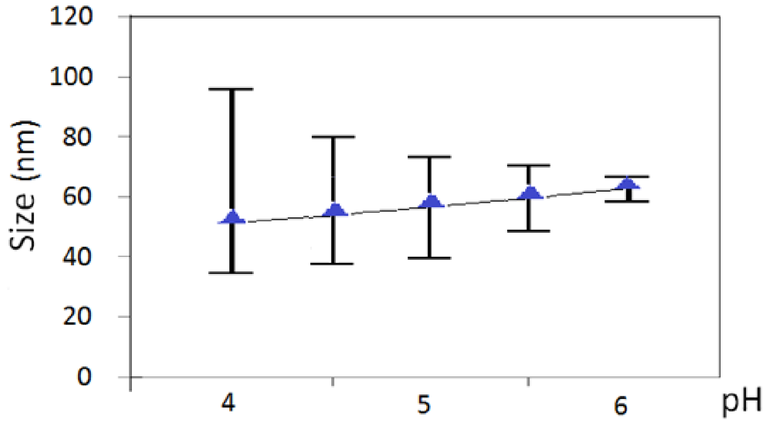

Fig. 2. Effect of pH on the size of lignin nanoparticles

Morphology of Alkali Lignin and Lignin Nanoparticles

A scanning electron microscope was used to study the morphology and approximate the particle size of LN to compare with those of AL. The AL and LN morphologies are shown in Fig. 3. Alkali lignin macromolecules have homogeneous and interconnected particles that are relatively uniform and flat. Lignin nanoparticles have an average diameter of less than 80 nm and highly porous surfaces.

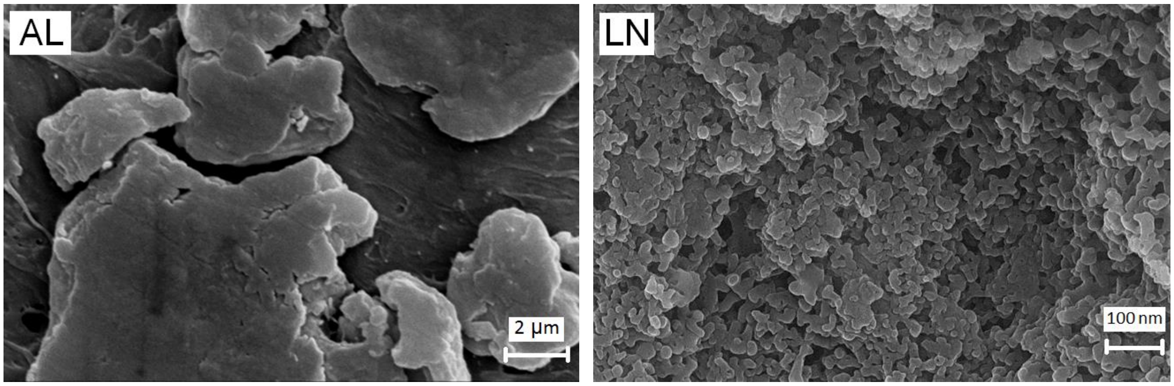

Fig. 3. Scanning electron microscope images of AL and LN compounds

FT-IR Spectra of AL and LN

The FT-IR spectra of AL and LN are shown in Fig. 4. The FT-IR spectra of AL and LN were very similar to each other. No change was seen in the chemical structure of AL in the process of creating nanoparticles. The FT-IR spectra of AL and LN are compared in Table 3.

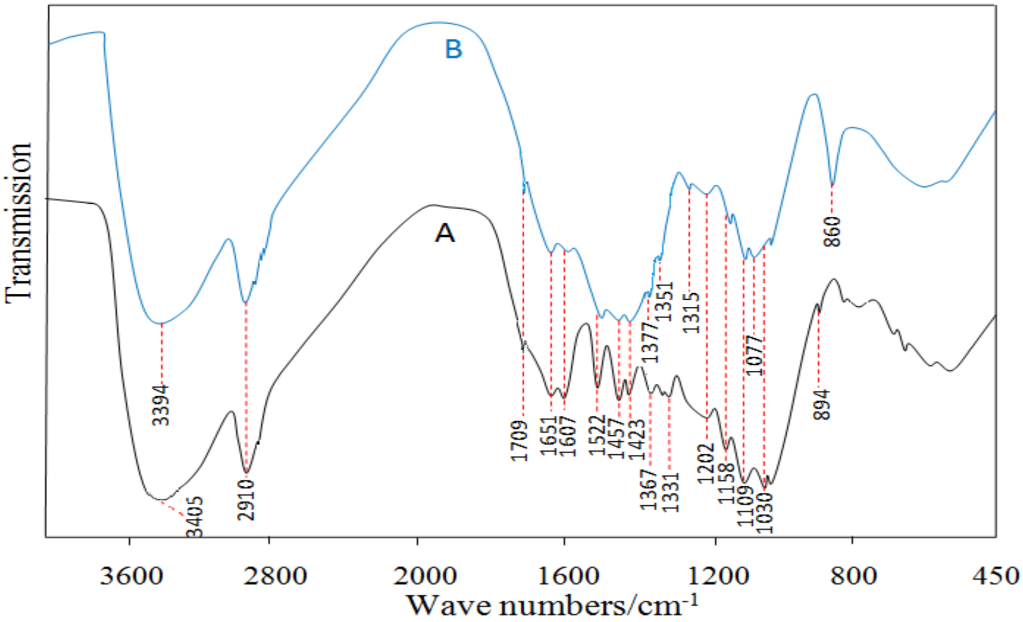

Fig. 4. FT-IR spectra of (A) alkali lignin and (B) nanolignin

The results show the stability of phenol propane rings in the synthesis of nanoparticles. The weak peak at 1,709 cm^{-1} shows the good vibration of carbonyl bonds in the carboxylic acid groups. The peak at 1,315 cm^{-1} in the LN shows the stretching vibration in connecting syringyl (S) and guaiacyl (G), which occurred as a result of nanoparticle formation. The stretching vibrations of S and G resulted in longer wavelengths of 1,377 cm^{-1} and 1,351 cm^{-1}. Furthermore, the absorption peak at 1,158cm^{-1} is a result of the -C-O vibration in para-hydroxyphenyl (H), which is more intense for LN than that of AL and was attributed to the interaction of -OH phenolic groups in H units. In the AL compound, the peak in the 3,405 cm^{-1} area relates to the vibration of -OH bonds. In LN the compound, these bonds are due to connections with ethylene glycol and caused the peak to move to 3,394 cm^{-1} and increase in intensity. The increased peak intensity at 1,077 cm^{-1} is attributed to overlapping -C-O vibrations in the connection of carboxylic acid groups with ethylene glycol and -C-H vibrations in connection with alcohol type 2. Zhang *et al.* (2016), reported similar information about extracting lignin from rice.

Table 3. Evaluation of FT-IR Spectra of Lignin and Nanolignin Compounds

Origin of Absorption Bands	Absorption Region (cm^{-1})	
	AL	LN
Stretching vibration of O-H in aliphatic and phenolic compounds	3405	3394
Stretching vibration of C-H bonds in CH_3 groups	2910	2910
Stretching vibration of -C=O in carboxylic acid groups (non-conjugated)	1709	1709
Stretching vibration of -C=O (conjugated)	1651	1651
Stretching vibration in the aromatic ring	1607	1606
Stretching vibration in the aromatic ring	1522	1517
Bending vibration of C-H bonds in CH_3 groups	1457	1457
Stretching vibration in the aromatic ring	1423	1421
O-H Bending vibration of phenolic and non-ether, stretching vibration in the S ring	1367	1377
Stretching vibration in the G ring	1331	1351
Stretching vibration of the bond between S and G	-	1315
Stretching vibration of C-O in alcohol type 1, C-O stretching vibration of S and G in the aromatic ring	1202	1202
Stretching Vibration of C-O in phenolic and carboxylic acid hydroxyls	1158	1158
Stretching vibration of C-H in units S, G, and H	1109	1109
Stretching vibration of C-H in alcohol type 2 and aliphatic ethers, stretching vibration of ether bonds between carboxylic acid groups in lignin and ethylene glycol in nanolignin	1030	1077

Thermal Stability

Thermogravimetric analysis (TGA) and differential thermogravimetry (DTG) spectra of AL and LN are shown in Fig 5. The DTG curves of the AL and LN are similar, which confirms that the chemical structure of AL remained unchanged in the process of creating nanoparticles. The DTG curve of AL is more intense than that of LN, which shows that the thermal decomposition of LN is intense. The weight loss of both AL and LN occurred in two stages. The first stage occurred between 38 and 141°C and resulted in a loss of 4.3%, which was attributed to the evaporation of water. The second occurred at a temperature of 141.5 °C and resulted in weight loss percentages of 51.2% and 47.7%, respectively. These losses were attributed to the breaking of the syringyl, guaiacyl, and p-hydroxyphenyl polymer units in the AL and LN (Meister *et al.* 1984; Zhang *et al*. 2016). The results showed that the presence of the ethylene glycol polar groups in AL increased the thermal stability of LN. With increased temperature, the ether bonds in the ethylene glycol are broken, preventing heat transfer to the main structure in LN. The greatest rate of thermal decomposition, for both AL and LN, occurred at a temperature of 361 °C.

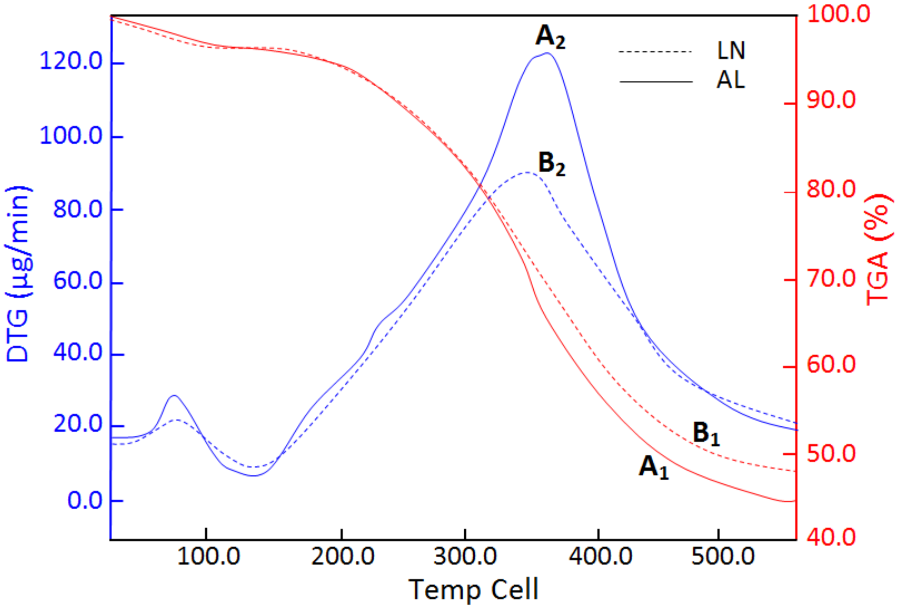

Fig. 5. TGA and DTG curves in the lignin (A_1 and A_2) and nanolignin (B_1 and B_2)

CONCLUSIONS

1. The present work demonstrates that alkali lignin can be successfully employed for the synthesis of lignin nanoparticles using acid precipitation technology.
2. The particle size obtained in the present work varied from 30 to 100 nm (*i.e.* number distribution), which was confirmed by DLS as well as SEM analyses.
3. FT-IR analysis showed the differences in the bonding pattern and the functional group.
4. The thermal behavior was analyzed through TGA-DTG analysis and indicated an improvement in the thermal stability of lignin in LN. Thus LN obtained from chemically modified lignin at relatively lower temperature can be effectively used as natural filler for polymer nanocomposite application.
5. The particular advantage of this approach is the absence of particle aggregation and formation of individual and randomly distributed nanoparticles. Furthermore, this method was facile and the process was completely green, which can be suitable utilized to further development of green nanoparticles synthesis on a large-scale.
6. Since LN is a renewable resource based material, it shows very good biocompatibility and zero toxicity to the environment.
7. The polar ends of LNP are vulnerable to chemical modifications, which can be additionally used as the path for the preparation of composites.
8. Lignin nanoparticles obtained from chemically modified lignin can be effectively used for polymer nanocomposite applications.

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