CELLULOSE CHEMISTRY AND TECHNOLOGY

SOLUTION PROPERTIES OF SOME MODIFIED LIGNINS

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In this paper, the behavior of modified/unmodified organosolv lignin (Alcell) solutions has been studied. Organosolv lignin was modified with different carboxylic acids, such as oleic, butyric, lactic acids and butyrolactone under cold plasma discharge. The modified lignins were characterized by particle size analysis and zeta potential measurements in water and alkaline solutions. It has been established that modification with different carboxylic acids, such as oleic, butyric, lactic acids, and butyrolactone under cold plasma discharge leads to structural and morphology changes of the solution properties for each kind of modified lignin. By cold plasma functionalization, solubility is changed, particle size and conductivity of aqueous solutions decrease, homogeneity decreases and zeta potential takes values close to the stability limit for dispersions. All these characteristics vary with the pH of solutions. In alkaline medium, the sizes of the lignin particles had a bimodal distribution, comparatively with the case of weak alkaline and acidic media. In acidic medium, the lignin associates had the greatest hydrodynamic values.

Keywords: lignin, carboxylic acids, butyrolactone, particle size analysis, zeta potential

INTRODUCTION

It has been demonstrated that lignin properties and applicability depend on its solubility and reactivity. Several examples of industrial utilization of sulfur-free, water-insoluble or soluble lignins have been presented.[1] Chemically modified lignins have been used as dispersing agent, complexing agent, flocculant, thickener or auxiliary agents for coating, paint or adhesives. Oil Well Drilling Muds Coal-water slurry dispersant, a lignin-derived material, has been reported to be a good dispersant for soils and applications have been shown for cleaning and/or laundry detergent compounds. A mixture including polycarboxylic acids and lignosulfonic acid has been used for cleaning aluminum plates to prevent calcium scaling. Dye dispersant was prepared from sulfate/sulfite pulping liquors cross linked with sulfite/formaldehyde. The products exhibit good dispersion property, heat-resistant stability, high temperature, dispersion property, fiber staining property and azo dye reducing property.

Lignosulfonates have been used as biodegradable and nontoxic emulsifiers or dispersants for emulsion or dispersion polymerization. Jet printing ink was prepared including sulfonated lignin. Lignin is used either directly or chemically modified, as a binder, dispersant agent for pesticides/herbicides, emulsifier, and as a heavy metal sequestrate.[2,3]

In our previous work,[4] lignin was modified under cold plasma conditions with carboxylic acids and butyrolactone in order to enhance its solubility and other physico-chemical properties to widen its application field by using modified lignin as dispersing agent, and to improve its compatibility with nonpolar polymers. These modifiers increase the hydrophylicity and functional groups of lignin and consequently the interaction with other polymers and with the environment. The average modification degree determined on the basis of XPS data varies in the order: LA (>4.3) < BL (11.7) < BA (13.3) < OA (17%). The significant changes in the thermal properties indicate that the modification by cold plasma affected also some bulk properties. This is mainly the case of the modification with butyric acid and butyrolactone. Cold plasma modification is an efficient and eco-friendly technique able to produce new valuable products from lignin, widening its compatibility with various polymers and also its applications. Testing new applications of these modified lignins requires knowledge of the solution properties.

It is known that Alcell lignin is soluble[5,6] in acetone, ethanol, methanol, and less soluble in acidic medium, N-methyl morpholine-N-oxide, dimethyl sulfoxide and N,N-dimethyl acetamide, ethylene glycol, guaiacol, cresols, and phenol. In a previous paper,[7] it has been shown that lignin separated from the hydrolyzate of the hydrothermal treatment of birch wood exhibits a particular behaviour in solution. These lignin aqueous solutions were structured, containing both nano- and micro-sized colloidal particles. The pronounced amphiphilic character of the lignin molecules governed their low critical micelle concentration values and enhanced the surface activity at the water-air and liquid-liquid interfaces. When decreasing the pH and increasing the ionic strength of the medium, the surface activity of lignin at the air-water interface grew, while that at the oil-water interface dropped.[7]

This paper deals with the study of the solution properties in water and alkaline medium of the lignin modified under cold plasma conditions with carboxylic acids and butyrolactone.

EXPERIMENTAL

Materials

Organosolv lignin (Alcell) (L) – fine brown powder soluble in ethyl alcohol, ethyl ether and chloroform – is a by-product of an organosolv pulping process called the Alcell process.[3] The organosolv lignin (Alcell lignin) used in this study has a number-average molecular weight of *Mn* ~1000, is highly hydrophobic and insoluble in neutral or acidic aqueous media, but soluble in moderate to strong alkaline solutions and certain organic solvents. Alcell lignin has a T*g* of ~130 °C.

Plasma treatment of lignin

Plasma treatment procedure has been previously presented.[4] Alcell lignin powder was impregnated with 5 wt% reagent solutions of oleic acid (OA), lactic acid (LA), butyric acid (BA) and butyrolactone (BL) in ethyl ether and deposited on a plasma reactor. This system was coupled to a plasma generator (500 Hz; 50 W). The discharge time was 60 min. After treatment, the product was removed from the reactor and the unbound reactive was extracted for 6 h in a Soxhlet extractor with ethyl ether and then the modified samples were dried and analyzed. Some of the sample characteristics are given in Table 1.

Investigation methods

The properties of the lignin solutions and the effect of chemical modification have been evidenced by particle size analysis and zeta potential measurements both in aqueous and alkaline solutions.

Table 1
Content of functional groups and degree of modification after grafting of the lignin samples under cold plasma conditions

Functional group (atomic percentage)*	Alcell lignin	Lactic acid grafted lignin	Oleic acid grafted lignin	Butyric acid grafted lignin	Butyrolactone grafted lignin
C=O or/and HO-C-OR	9.39	10.71	19.40	17.49	15.47
O–C=O	1.27	2.00	2.96	1.58	1.30
O–H	20.96	20.06	17.40	18.17	23.42
Average modification degree (%)	-	> 4,3	17	13.3	11.7

* determined by X-ray photon spectroscopy (XPS)

Particle size analysis of the polymeric samples was done by the dynamic light scattering (DLS) technique with a Zetasizer model Nano ZS device (Malvern Instruments, UK) with a red laser (wavelength of 633 nm, He/Ne). The system uses non-invasive back scatter (NIBS) technology wherein the optics are not in contact with the sample, back scattered light being detected. The use of NIBS technology reduces multiple scattering effects and consequently size distributions in higher concentrations of the sample can be measured. Mie method was applied over the whole measuring size range from 0.6 nm to 6 μm. Dynamic light scattering (DLS) measurements were performed to obtain the Z-average distribution of the apparent hydrodynamic diameter (D_H) of the aggregates using the equation:

$$D_H = \frac{kT}{3\pi\eta D} \tag{1}$$

where: D_H is hydrodynamic diameter, k is Boltzman constant, T - temperature, η – viscosity, D – diffusion coefficient.

The cumulated analysis gives: Z-Average size, a mean value for the size, and a width parameter known as the polydispersity or the polydispersity index (PDI). It is important to note that this mean size (hydrodynamic diameter, often given the symbol Z or z-average) is intensity mean. It is not a mass or number mean because it is calculated from the signal intensity.

Determinations have been done on dilute solutions of modified lignins at different pHs of 1-10 in the concentration interval of 1.25-8 mg/mL. The molecular weight and the second virial coefficient (A_2) of the polymeric samples were also determined using the Zetasizer Nano ZS instrument, based on the measurements of static scattered light (SSL) intensity for various concentrations of sample at one angle (173°).

The plot of KC/R_θ versus C is expected to be linear with an intercept equivalent to 1/M and a slope equal to the second virial coefficient A_2. The following relations (Rayleigh equation) are valid:

$$\frac{KC}{R_\theta} = \left(\frac{1}{M} + 2A_2C\right)P(\theta) \tag{2}$$

where:

$$K = \frac{2\pi^2}{\lambda_0^4 N_A}\left(n_0\frac{dn}{dc}\right)^2 \tag{3}$$

$$P(\theta) = 1 + \frac{16\pi^2 n_0^2 Rg^2}{3\lambda_0^2}\sin\left(\frac{\theta}{2}\right) \tag{4}$$

and

$$R_\theta = \frac{I_A n_0^2}{I_T n_T^2} R_T \tag{5}$$

where: K – optical constant, M – molecular weight, A_2 – 2nd virial coefficient, C – polymer concentration, R_θ – Rayleigh ratio of the sample, $P(\theta)$ – shape factor; n_o – refractive index of the solvent at the laser wavelength, N_A – the Avogadro constant, and dn/dc is the refractive index increment of the scattered species in the solvent. R_g – radius of gyration; θ – measurement angle, I_A – intensity of sample, I_T – intensity of standard (toluene), n_T – refractive index of standard (toluene), R_T – Rayleigh ratio of standard (toluene).

The Rayleigh ratio (R_θ) is the ratio of scattered to incident light intensity. The intensity of incident light interacting with the macromolecule is difficult to measure. Therefore, the standard approach is to measure the scattering intensity of the analyte relative to that of a well described standard with a known Rayleigh ratio (for toluene at 633 nm the Rayleigh ratio is 1.3522×10^{-5} cm^{-1}).

Zeta ζ potential measurements

The zeta potential of 1% lignin solved in 0.1M NaOH (ζ) was recorded on Zetasizer Model Nano ZS equipment provided by Malvern Instruments, UK. The zeta potential was estimated with the Smoluchowski relationship from the electrophoretic mobility (μ), according to the equation:

$$\zeta = \frac{\eta\mu}{\varepsilon}, \text{ with the condition } k\alpha \gg 1 \tag{6}$$

where with η is viscosity, ε is the dielectric constant, and k and α represent the Debye-Hűckel parameter and particle radius, respectively.

Each zeta potential value represents an average of three recordings. A constant temperature of 25 ± 0.02 °C was maintained, using the internal thermostat of the system. Also, the difference between the measurements and their average is less than 2.5%. Following the determination of zeta potential (ZP), the conductivity was also estimated.

During the size distribution and zeta potential determination, the pH was adjusted with 0.1 M HCl or 0.1 M NaOH solutions, using an Autotitrator Malvern MPT2 device, which works as an external component for the Zeta Sizer Nano ZS equipment. The autotitrator device is equipped with a stirring system with 75 rpm. The solutions were subjected to mechanical stirring in a bath before the measurements. The working temperature was 22 °C and it was maintained constant (±0.1 °C) with a Peltier device. The size distribution was recorded on the same device based on dynamic light scattering (detected at a back scattering angle of 173°). The emitter is represented by the red laser at 632.8 nm (He/Ne).

RESULTS AND DISCUSSION

Particle size analysis and zeta potential results

As already mentioned, the weight average of molecular weight has been determined by light scattering measurements, using solutions of different concentrations varying between 1.25 and 8 mg/mL. The results are given in Table 2.

The data of Table 2 indicate that the weight average of molecular weight of Alcell lignin is not influenced too much by the modification with lactic acid (LA) and oleic acid (OA), but it is drastically decreased by modification with butyric acid and butyrolactone. In the last two cases, the molecular structure of lignin is partially destroyed. The modification of the lignin with carboxylic acids also leads to a significant increase of the second virial coefficient, which means increased interaction with the solvent (water) because of carboxylic groups incorporation by cold plasma exposure in the presence of carboxylic acid modifying reactants, while in the case of butyrolactone use for treatment, the second coefficient takes negative values, the interactions with the solvent being minimized, they probably become repulsive because of ester groups formation, as it was shown in a previous paper by FT-IR spectroscopy results.[7]

Dalimova's studies on particle size distribution, conductivity and zeta potential performed both in water and NaOH solutions revealed the specific behavior of hydrolyzed lignin in both media.[8]

Such studies have been also conducted on cold plasma modified lignins.

Aqueous solutions

The distribution curves for particle size (Fig. 1) and zeta potential results (Fig. 2) show a clear differentiation between unmodified and modified lignin. Particle size distribution curves are bimodal in all cases, but the main peak of unmodified lignin is narrower than those of modified lignin. The Z-values of 150-400 nm are characteristic for the first peak, while those for the second one Z ranges from 800 to 6500 nm. The average values evaluated from these curves are given in Table 3.

Table 2
Average molecular weight and second virial coefficient for lignin and plasma modified lignin samples

Sample	Mw (kDa)	A_2 (mL·mol·g^{-2}) 10^3
L	15.62	1.04
L/LA	13.53	3.79
L/OA	13.59	2.39
L/BA	7.22	4.35
L/BL	2.32	-1.81

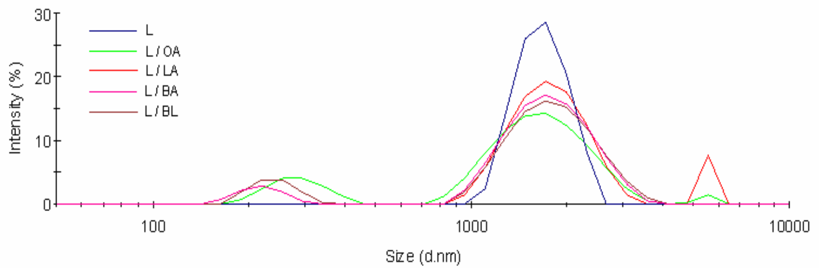


Figure 1: Particle size distribution of L and cold plasma modified lignins

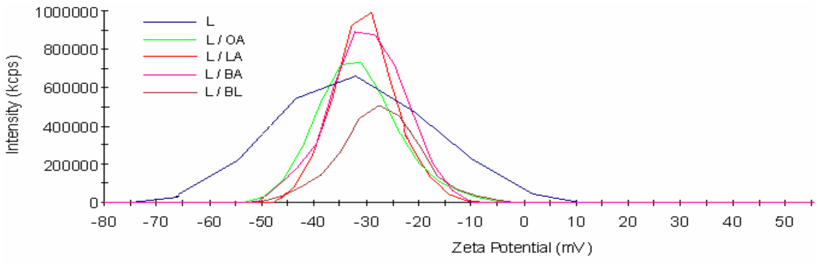


Figure 2: Zeta potential distribution of L and cold plasma modified lignins

Table 3
Particle size analysis, zeta potential and conductivity of Alcell lignin and lignins modified with carboxylic acids and butyrolactone in water at pH = 5.5

Sample	Z-average (nm)	PDI	Average zeta potential (mV)	Conductivity (mS/cm)
L	1850	0.245	-33.2	0.0510
L/LA	1220	0.434	-31.5	0.0120
L/OA	1150	0.502	-30.2	0.0359
L/BA	1260	0.317	-29.9	0.0330
L/BL	1310	0.431	-27.4	0.0324

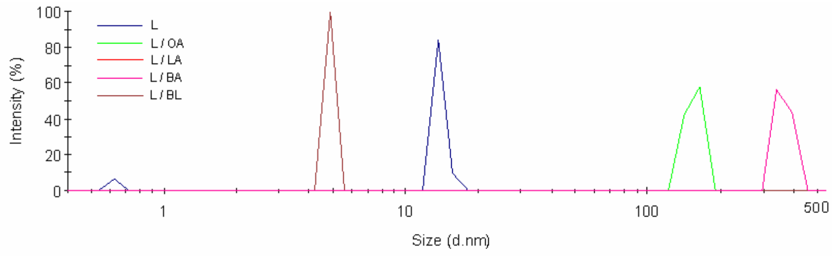


Figure 3: Particle size distribution of L and cold plasma modified lignins at pH = 1.81

It can be easily remarked that Z-average decreased after cold plasma modification, the decrease is very important for the samples treated with carboxylic acid for which Z-average decreased with ~600-700 nm, while in the case of the samples treated with butyrolactone the decrease is of 540 nm. All samples become more heterogeneous after cold plasma modification; polydispersity index increases twice.

The distribution curve for Z potential of the unmodified sample (L) (Fig. 2) is very large with a wide maximum, which ranges from -45 to -5 mV. The curves corresponding to cold plasma modified lignins are narrow with maximum for carboxylic acids modified lignins at ~ -37 mV, while that corresponding to butyrolactone modified lignin is placed at 27 mV (Fig. 2). Both average value of zeta potential and conductivity decreased after cold plasma modification of lignin (Table 3). All these characteristics clearly indicate that modification of lignin both with carboxylic acids and butyrolactone took place under cold plasma conditions and that their dispersion in water is better and stable than that of unmodified lignin. All these results indicate that plasma treatment occurred in bulk and was not limited to the surface.

NaOH solution

Unmodified lignin solution and modified lignin solution (L/OA) were dissolved in 0.1 M NaOH solution under slow magnetic stirring. The solubility of lignin in 0.1 M NaOH solution was improved with respect to that in water, but it was lower than that in acidic medium. During the change of solution pH with 0.1 M HCl, the transition from a clear solution to a dispersion of lignin particles was observed. The process was most evident on modified lignin samples. Before the size determinations, all solutions were magnetically stirred and/or ultrasonicated. Changes in solubility with pH decrease were revealed by measurements of particle size analysis, namely by increasing both the particle size and polydispersity index. Also, the solutions became a little unclear. In the case of the unmodified lignin solution, the dispersion formation was observed at pH 2.5, while for the solutions of modified lignin a precipitate appeared at pH 4.3. In addition, at acidic pH the zeta potential decreased for all samples, according to Table 4, pointing out the interaction between unmodified and modified lignin particles in acid environment, followed by the decrease in the system stability.

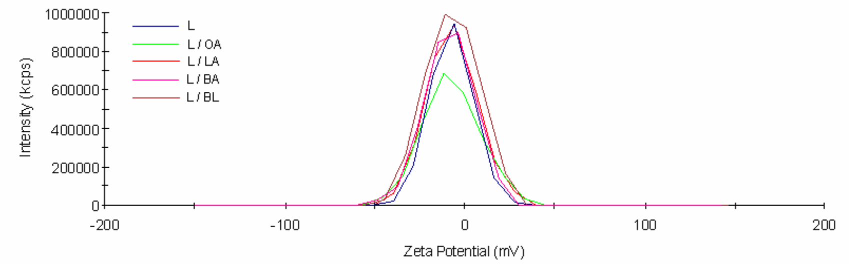
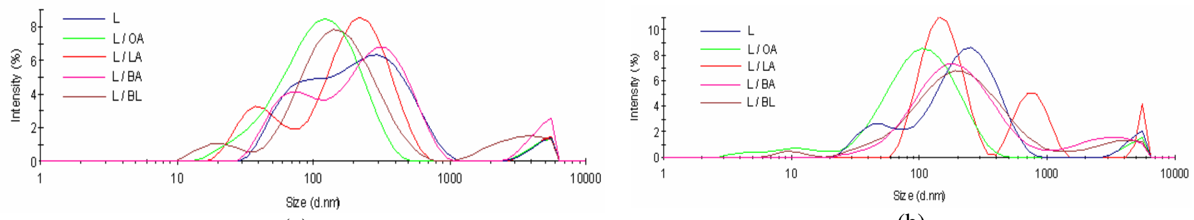


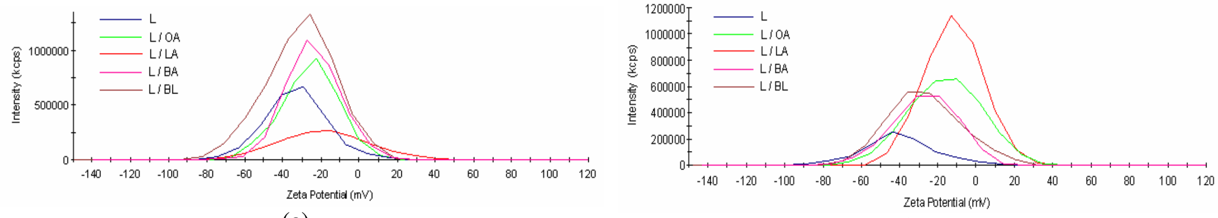
Figure 4: Zeta potential distribution of L and cold plasma modified lignins at pH = 1.81



(a)

(b)

Figure 5: Particle size distribution of L and cold plasma modified lignins at pH = 7 (a) and pH = 10.6 (b)



(a)

(b)

Figure 6: Zeta potential distribution of L and cold plasma modified lignins at pH = 7 (a) and pH = 10.6 (b)

In acidic medium, the particle sizes are smaller and the samples are better individualized with respect to their nature, mainly at low pH such as pH 1.8 (Fig. 3), but not regarding zeta potential distribution (Fig. 4). Zeta potential distribution curves are similar for all samples. At a low pH value (1.81), the carboxylic acids modified lignins have bigger particles (200-500 nm) than unmodified lignin (6-8 nm) and butyrolactone modified lignin.

At higher pH (pH 4-10), the particle size distribution for most samples becomes more complex (Fig. 5) with at least three peaks, with the exception of L/OA sample whose dimensions remain unchanged for pH > 4. Probably, in this case, the modification took place mainly on the surface, lignin became hydrophobic and its interaction with the solvent or surrounding molecules was weak. In a strong alkaline medium, the sizes of the lignin particles had a bimodal distribution and showed the lowest values, comparatively with the case of weak alkaline and acidic media, in which the lignin associates had the greatest sizes and a polymodal distribution.

At a pH > 5.5, the zeta potential of the modified lignins was superior to that of unmodified lignin (Fig. 6), but it was lower compared to that of the solution with low pH. There was also a certain fraction of particles with the zeta potential situated beyond the stability limits for dispersions, especially for unmodified lignin. However the average zeta potentials of modified lignins did not exceed the stability limits (+30 - -30mV).[9-11]

The dependence of particle size, zeta potential and conductivity on pH may be deduced from the examination of the data presented in Table 4 and Figures 7 and 8. Z-average shows very high values at pH 1.8 (Table 4), and then at higher pH (pH>4.6). It increases with increasing pH for all samples excepting L/OA for which the particle size presents an insignificant variation. The lowest values are recorded for L/OA sample.

The polydispersity of soluble lignins probably results from the degradation of their tri-dimensional structure, as well as from the pronounced aggregation of low molecular weight units.[12-14] Therefore, producing lignins with lower polydispersity by cold plasma modification with carboxylic acids could be of interest. Zeta potential decreases with increasing pH up to pH 10, as can be seen in Figure 8. The lowest zeta potential values are characteristic of the unmodified lignin sample and the highest to L/LA sample. It can be concluded that the cold plasma modified samples show better stability than the unmodified lignin sample. PDI values increase with increasing pH, the dispersion being more heterogeneous. The conductivity decreases with increasing pH up to pH ~6 and then remains constant.

Table 4
Particle size analysis, zeta potential and conductivity of Alcell lignin and lignins modified with carboxylic acids and butyrolactone at various pHs

Sample	Solvent/pH	Z-average (nm)	Zeta potential (mV)	PDI	Conductivity (mS/cm)
L	pH = 10.7	151	-39.5	0.488	12
	pH = 7.31	136	-32.9	0.511	12
	pH = 6.95	142	-33.2	0.468	12
	pH = 4.66	111	-26.5	0.517	12.1
	pH = 1.85	1080	-7.31	0.567	20.2
L/LA	pH = 10.6	282	-11.9	0.505	11.7
	pH = 8.57	149	-16.2	0.629	11.8
	pH = 6.91	119	-18.5	0.492	11.9
	pH = 4.58	76.9	-24.3	0.627	12.1
	pH = 1.81	1280	-6.85	0.335	21.9
L/OA	pH = 10.6	81	-16.2	0.449	11.9
	pH = 8.52	82.3	-20.9	0.429	11.9
	pH = 7.01	86.9	-25.7	0.444	11.9
	pH = 4.61	88.5	-24.9	0.424	12
	pH = 1.82	8840	-7.32	0.528	23.2
L/BA	pH = 10.7	168	-26.7	0.466	10.4
	pH = 8.76	174	-27.0	0.762	10.3
	pH = 7.05	144	-24.3	0.718	10.4
	pH = 4.82	97.7	-22.3	0.713	10.6
	pH = 1.96	7750	-8.54	0.556	16.6
L/BL	pH = 10.7	162	-26.9	0.481	12.1
	pH = 7.04	114	-30.5	0.592	12.1
	pH = 6.2	117	-25.8	0.648	12.1
	pH = 4.8	92.4	-24.9	0.873	12.3
	pH = 1.8	1184	-6.91	0.319	20.3

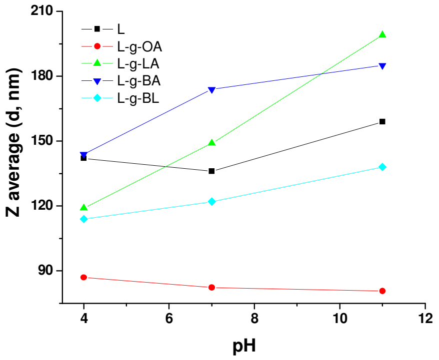


Figure 7: Z-average *vs* pH of solutions of L and cold plasma modified lignins

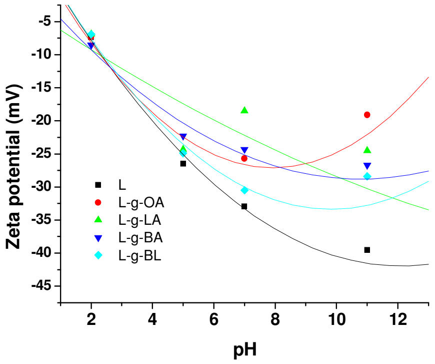


Figure 8: Zeta potential *vs* pH of solutions of L and cold plasma modified lignins

CONCLUSION

By cold plasma functionalization, the solubility of lignin in aqueous and alkaline solutions was improved, particle size was decreased and zeta potential took values close to the stability limit for dispersions. The cold plasma modified samples showed better stability than the unmodified lignin sample. Polydispersity index values increased with increasing pH, the dispersion being more heterogeneous. In a strong alkaline medium, the sizes of the lignin particles had a bimodal distribution and showed the lowest values, comparatively with the case of weak alkaline and acidic media, in which the lignin associates had the greatest sizes and a polymodal distribution.

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