JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 9, No. 4, April 2007, p. 970 - 974

Natural polymer modification under radio-frequency electrical discharge conditions

G. CAZACU*, M. TOTOLIN, G. CONSTANTINESCU, D. CIOLACU
"Petru Poni" Institute of Macromolecular Chemistry, 41 A Grigore Ghica Voda Alley, Iasi, Romania

Chemical modification of natural polymers (insoluble lignin and cotton cellulose) in radio-frequency cold plasma has been investigated. The treatments of polymers were carried out in a rotator cold plasma installation specially designed for the R. F. plasma treatment of powdery materials (i.e. insoluble lignin) and in a statically R.F. plasma device for cotton cellulose. Spectral, physical and chemical analysis proved the formation of the new products with improved properties.

(Received November 2, 2006; accepted February 28, 2007)

Keywords: Plasma, Lignin, Cellulose, Natural polymer, Radio-frequency cold plasma

1. Introduction

During 1980-2000 years have seen increasing interest in the use of plasma for in situ polymer synthesis and surface modification of the synthetic or natural polymers [1,2, 3]. Plasma is defined as a partially ionized gas composed of electrons, ions, atoms and molecules in excited and ground states.

Radio-frequency (RF) reactors are most commonly used for synthesis and surface modification of various substrates. RF plasmas can be sustained even by using insulated electrodes located inside or outside the reaction chamber and under lower pressure conditions. The energies of sample-bombarding ions of RF plasmas can conveniently be controlled by adjustable self-bias. The advantages of RF plasma chemistry approaches can be summarized as:

- It involves only a very thin surface layer of the substrates exposed to the discharge (around 10 nm into plasma-enhanced modification processes); the bulk of the material remains practically un-modified.
- It is dry chemistry and accordingly it do not require the use of large amounts and often toxic of organic chemicals that carry potential environmental hazards.
- The energy levels of plasma species are comparable with the common bond energies, and as a consequence even the most inert material surfaces can be conveniently altered.

Lignocellulosic materials are composed from three main compounds: cellulose, lignin and hemicelluloses. Lignin represents the main aromatic component of the higher plant tissues; it represents about 20-40 wt% of mass of vegetable biomass composition, to compete with cellulose as spread and accessibility. From chemical point of view, term lignin refers to a family of heterogeneous biopolymers that contain limited branching and/or crosslinking, whose content is variable as a function of woody species from which is isolated [4]. Lignin also is characterized by different functional groups which can be used to carry out modification reactions, or which can be involved in the establishing of bonds with other components of wood [5, 6]. The functional groups attached to the basic phenylpropanoid skeleton include phenolic hydroxyl, aliphatic hydroxyl, carbonyl, methoxyl groups. Lignin is a potential raw material, with very limited uses, due to its complicated chemical structure. Classical attempts to modify lignin through common chemical reactions in order to transform it in useful goods resulted in fewer applications only [7,8].

Plasma treatments, in presence of some monomers, can be utilized to improve the properties and utility of lignin in a great number of applications (compatibility, bonding and adhesion with another polymers) [9,10].

Also, an appreciable number of attempts to carry out chemical modifications of cellulose, the main compound of the wood, have been reported with the aim to obtain new products with special properties. Plasma conditions offer the possibility of generating active species on cellulose fibers also, determining later graft formations [11].

The simultaneous appearance of macroradicals on lignin and cellulose supports, monomer homopolymerization and grafting reactions are the main processes in radio-frequency electrical discharge conditions.

This paper presents the possibility of surface modification and/or grafting the lignin with methyl methacrylate and acrylonitrile and cotton cellulose with acrylamide in R. F. cold plasma conditions, in order to improve the properties of supports.

2. Experimental

2.1. Materials

Powder lignin (L) obtained from furfural lignocellulosic by acid hydrolysis. High purity methylmethacrylate (MMA) and acrylonitrile (AN), purchased from Aldrich Chemical Co, were used as grafting monomers for lignin.

Fiber cotton celulose (1.8 den) has been previously extracted with ethanol/benzene 1/1 vol., 70^0C, in order to remove ingredients. Acrylamide was purchased from Eastman Organic Chemicals Co.

2.2. Methods

The grafting of lignin has been run in a R. F. cold plasma reactor specially designed for treatments on powdery materials (Fig. 1).

The support (lignin) was introduced into Pyrex rotator glass cylindrical shaped vacuum tight plasma reactor (13), with 1 liter volume; after five washing cycles with nitrogen gas and with selected gaseous – phase monomers (methylmethacrylate or acrylonitrile) the working pressure in the system was established (1.5 mm Hg) and then the power was dissipated to the reactor through the semi-cylindrically, external, silver coated electrodes (6). The power of plasma (0 – 5 kW) was assured by a R. F (frequency 13.6 MHz) generator (7). The monomers were continuously distilled from the monomer flask (11) into the reactor during the development of the grafting processes (reaction time - 1 hour).

Inert gas plasma (nitrogen plasma) control reactions, in the absence of monomers and in the same conditions, carried out, parallel to the main experiments.

Modified lignins were extracted with chloroform (for methylmethacrylate) or dimethylformamide (for acrylonitrile), 24 hours, room temperature. Insoluble fraction (mixture of grafted lignin and lignin) was investigated, before and after hydrolysis with 5 % NaOH solution (2 h, t = 100^o C).

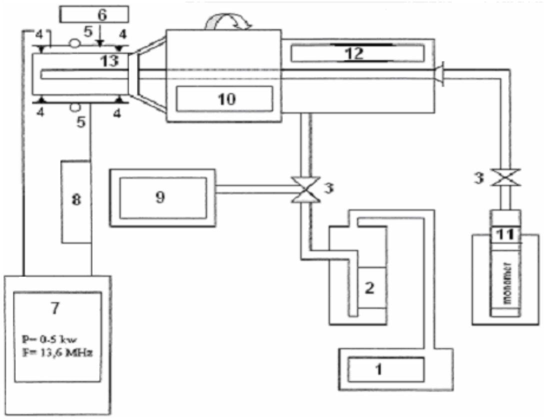


Fig. 1. R. F. rotator cold plasma reactor:
1 – vacuum pump; 2 – cold trap; 3 – glass valves; 4 – PTFE sustaining systems for electrodes; 5 – PTFE ring; 6 – semi- cylindrically external silver coated electrodes; 7 – RF plasma generator; 8 – wire connections; 9 – Penning Pirani vacuummeter; 10 – rotator electrical engine; 11 – monomer flask; 12 – glass chamber; 13 – cylindrically vacuum plasma reactor (neutral Pyrex glass, V = 1 liter).

In another experiments cellulose fibers were deposited on glass supports, immersed for 5 h in 10 % acrylamide solution and dried, and glass support was introduced in plasma reactor (Fig. 2), reaction time 10 minutes, power 250 W.

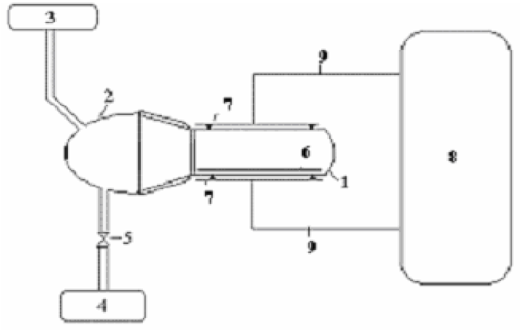


Fig. 2. Cold plasma installation for cellulose grafting:
1 - cylindrically shaped vacuum plasma reactor (neutral Pyrex glass, L = 30 cm, ∅ = 4 cm); 2 – close glass vacuum system; 3 – vacuum meter Penning Pirani; 4 – vacuum pump; 5 – glass valves; 6 – glass support (15 X 100 mm); 7 – semi- cylindrically external silver coated electrodes; 8 – RF generator (250 W, 13.56 MHz); 9 – wire connections.

2.3. Investigation methods

In order to prove the formation of graft copolymers in cold plasma conditions, the extracted and dried final samples were analyzed using FT-IR spectroscopy, ^{1}H-RMN, DTA, microcalorimetry, scanning electron microscopy (SEM) and alkaline hydrolysis.

3. Results

The vinyl monomer grafted lignin (insoluble fraction) was investigated by spectral measurements (IR), chemical methods (elemental analysis, methoxy group determinations), SEM, DTG and calorimetric data.

Fig. 3 presents IR spectra of standard lignin, inert (N2) plasma treated lignin (L_{inpl}), methylmethacrylate grafted lignin (insoluble fraction) (PMMA-g-L)$_i$ and poly(methylmethacrylate) (PMMA).

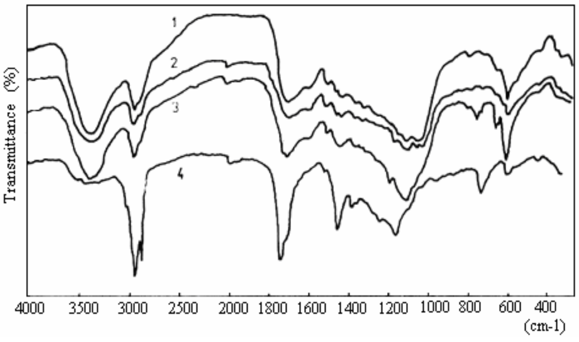


Fig. 3. IR spectra of control lignin (1), inert (N2) plasma treated lignin (2), PMMA-g-L_i (3); PMMA (4).

In the spectrum of the methylmethacrylate grafted lignin (insoluble fraction) (3) can be noticed important changes in comparison with the control compound (1) and inert plasma treated lignin (L_{inpl}) (2). Thus, besides the adsorption maxima peculiar to the insoluble lignin (3500 cm^{-1}, ν OH phenolic; 2950 and 2870 cm^{-1}, ν CH aromatic and aliphatic; 1720 cm^{-1}, ν C=C conjugated and ν C=O; 1620 cm^{-1} and 1500 cm^{-1}, ν CH aromatic; 1450 and 1320 cm^{-1}, ν CH saturated aliphatic; 1120 cm^{-1}, ν O-CH_3 and 1020 cm^{-1}, ν OH aliphatic) characteristic vibrations for poly(methylmethacrylate) appear in the spectrum of grafted copolymer (3): 1723 cm^{-1}, ν C=O and ν OCH_3; 1000 – 1380 cm^{-1} ν C-O-C; 826 and 745 cm^{-1}, carbon backbone chain vibrations from poly(methylmethacrylate).

The IR spectra of the acrylonitrile grafted lignin (PAN-g-L) in comparison with the control lignin, the inert plasma treated lignin and poly(acrylonitrile) are presented in Fig. 4.

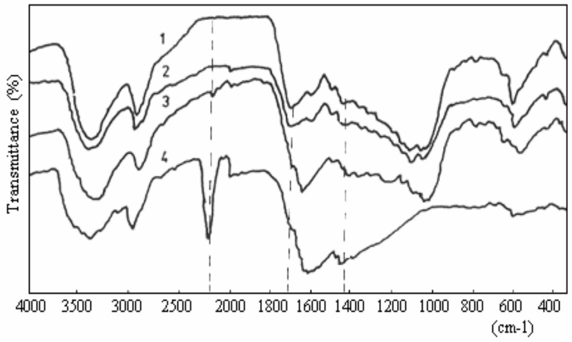


Fig. 4. IR spectra of control lignin (1), inert plasma treated lignin (2), acrylonitrile grafted lignin (3) and poly(acrylonitrile) (4).

One can notice that the grafted copolymer presents, besides the absorptions specific to lignin, a new peak (2200 cm^{-1}) due to the vibration of ν C≡N group.

The elemental analysis data of the grafted lignin, control lignin and inert plasma treated lignin (L_{inpl}) and lignin grafted products are presented in Table 1.

Table 1. The elemental analysis data (%).

Atoms	L	L_{npl}	PMMA-g-L	PAN-g-L
C	53.05	53.08	53.61	55.05
H	5.73	5.92	5.39	5.13
O	41.22	41.00	41.00	36.41
N	0	0	0	3.41

Because of the surface modification processes, major changes in the carbon, hydrogen and oxygen contents, after the grafting reactions cannot be practically evidenced. Important differences appear however in the OCH_3 group content and the nitrogen content of PAN-g-L. The nitrogen content (3.4 %) and the decrease of the number of OCH_3 groups (from 3.6 % to 3 %) in the PAN-g-L and the relatively slight increase of the OCH_3 content in the case of PMMA-g-L, indicate that the grafting processes took place under cold plasma conditions.

Elemental analysis data and OCH_3 group contents permitted to establish the empirical formula of the products:

L	$C_{8.00}H_{9.74}O_{4.50}(OCH_3)_{0.22}$
L_{ipl}	$C_{8.00}H_{10.24}O_{4.54}(OCH_3)_{0.22}$
PMMA-g-L	$C_{8.00}H_{9.18}O_{4.49}(OCH_3)_{0.23}$
PAN-g-L	$C_{8.00}H_{8.54}O_{3.88}(OCH_3)_{0.16}N_{0.43}$

In order to obtain more proofs for the formations of the plasma grafted copolymers, mild alkaline hydrolysis (5 % NaOH solution, refluxing conditions for 2 hours) were carried out on insoluble fraction (plasma grafted copolymers) with the aim of cleaving the support (lignin) from the grafted copolymers and of establishing their chemical structures. Control hydrolysis experiments were performed on the standard lignin in the same time.

By hydrolysis of grafted copolymers resulted two fractions for all the samples: soluble and insoluble. Table 2 presents the relative ratios of the soluble and insoluble fractions.

Table 2. The relative ratios of soluble and insoluble fractions resulted from hydrolysis experiments.

Samples	Soluble fraction (%)	Insoluble fraction (%)
Lignin	41.50	58.50
PMMA-g-L	34.91	65.09
PAN-g-L	19.66	80.34

It can be noticed that the plasma grafted compounds are much more stable to the alkaline solubilization processes.

The structural analysis (IR, NMR and elemental analysis) of both fractions resulted from methylmethacrylate grafted lignin and acrylonitrile grafted lignin emphasizes, once again, the formation of the grafted copolymers. Thus, IR spectra of the soluble fractions present the absorptions specific to the corresponding homopolymers of methylmethacrylate and acrylonitrile respectively; on the other hand the FT-IR spectra of insoluble fractions are similar to the FT-IR spectrum of control lignin.

Similar statements arise on the basis of NMR analysis (Fig. 5).

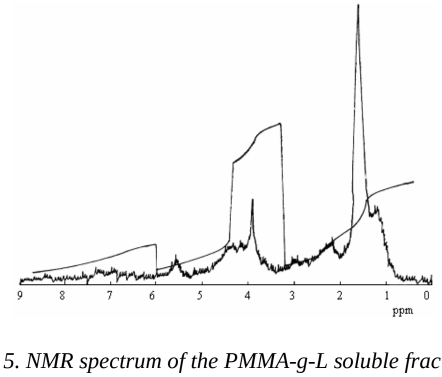


Fig. 5. NMR spectrum of the PMMA-g-L soluble fractions.

NMR spectrum evidences the presence of absorptions with low intensity corresponding to the OCH_3 groups (3.6 ppm), the appearance of the "unsaturated" absorptions in the field of 5-6 ppm and the existence of bound and/or incorporated lignin fragments (6.5-8 ppm). These can be explained by plasma-destruction processes (partial splitting of the OCH_3 groups), and probably by the dehydrogenation and oxidation reactions.

Elemental analysis data show minor modifications in the atomic compositions of insoluble fractions (Table 3).

Table 3. The elemental analysis data of insoluble fractions (%).

Elements	L	PMMA-g-L_i	PAN-G-L_i
C	56.84	57.59	55.66
H	5.57	6.07	5.47
O	37.59	36.34	36.12
N	0	0	2.63

After hydrolysis a 2.68% nitrogen content remains in the case of insoluble fraction from PAN-g-L, fact which proves the chemically bound poly(acrylonitrile) to the lignin.

The existence of the graft layers on the surfaces of the lignin particles is clearly evidenced by scanning electron microscopy, important morphological differences being observed between the support and the grafted compounds (Fig. 6).

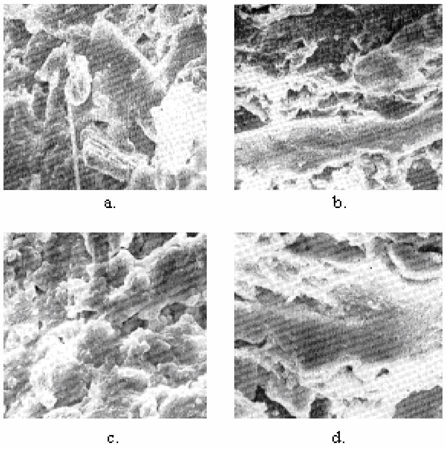


Fig. 6. Scanning electron micrographs of control lignin (a), inert plasma treated lignin (b), methylmetacrylate grafted lignin (c) and acrylonitrile grafted lignin (TESLA SP 500 apparatus; x 3000).

Indirect evidence for the formation of the grafted copolymers is supplied by DTG and calorimetric data (Table 4).

Important changes in the patterns of the DTG diagrams of the acrylonitrile grafted lignin appear in comparison with the control lignin, however the thermooxidative behavior of the methylmethacrylate grafted lignin is almost similar to that of the support. The wetting heats (ΔH) of the samples show important modifications only for acrylonitrile grafted lignin.

Table 4. Thermal behavior and wetting heats (ΔH) of the lignin grafts under cold plasma conditions.

Samples	Ti °C	Tm °C	n	Ea Kcal/mol	ΔH Cal/g
L	173	265	0	16.00	5.65
L_{inpl}	130	265	0	12.00	5.93
PMMA-g-L	172	270	0	17.00	5.85
PAN-g-L	205	300	0	18.00	6.35
PMMA	240	334	2.5	43.00	-
PAN	275	313	0	7.75	-

In order to prove the formation of graft copolymers of cotton cellulose in radiofrequency electrical discharge conditions, the extracted final samples were investigated.

In Fig. 7 the FT-IR spectra of the acrylamide grafted cotton fibres and poly(acrylamide) in comparison with the standard material are presented.

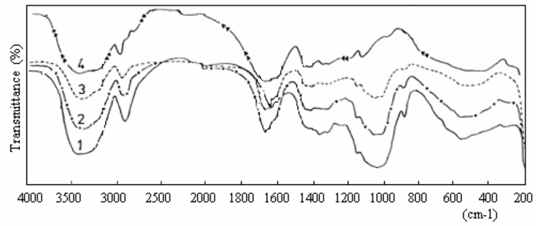


Fig. 7. Comparative IR data - cotton cellulose (1); acrylamide grafted copolymers (2) and (3); polyacrylamide (4).

One can notice that the grafted copolymers (2 and 3) present, besides all the absorptions specific to the cellulose, vibrations due to the grafted structures: 3182 cm^{-1} (ν CO-NH-CO), 1660 cm^{-1} (ν NH), and 1450, 1410 cm^{-1} (ν –CO-NHR).

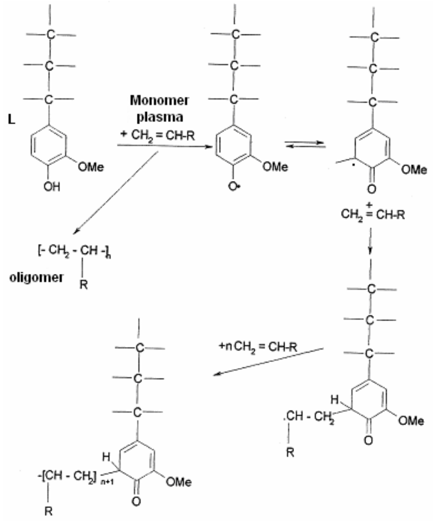
The thermal behavior of grafted cotton cellulose (PAA-g-C), in comparison with that of the cellulose standard (C), as well as the physical mixture of cotton cellulose and poly(acrylamide) are presented in Table 5.

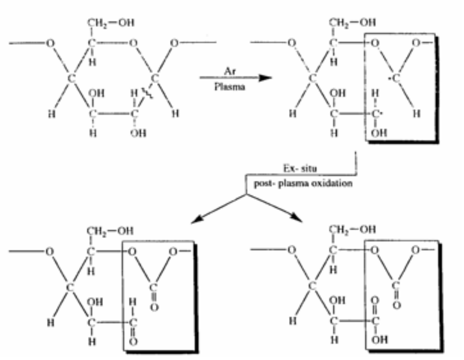
Table 5. Thermo-oxidative destruction behavior of grafted cotton cellulose (PAA-g-C), standard cellulose (C) and physical mixture cellulose+ poly(acrylamide).

Sample	Peak I		Peak II		n	Ea kcal/ mol
	Ti °C	Tm °C	Ti °C	Tm °C		
C	210	338	388	420	0.9	23.79
PAA-g-C	210	352	449	548	0.8	22.33
Physical mixture: C+PAA	200	335	450	565	0.5	20.25

Important differences between the thermal destruction zones for support polymer and the grafted product are pointed out. The values are, however, close to the data recorded for poly(acrylamide) and cellulose physical mixture.

The suggested plasma induced reaction mechanisms for modification of lignin and cotton cellulose fibers are shown bellow:





4. Conclusions

- Plasma treatments of insoluble lignin and cellulose have been successfully accomplished.
- Radio-frequency electrical discharges are suitable to graft lignin in acrylic monomer plasma and also for treatments of predeposited acrylamide on the surface of cellulose fibers.
- Spectral, physical and chemical analyses prove the graft–copolymers formation and polymeric nature of the grafts.
- The grafting processes develop on the material surfaces only.
- Two reaction mechanisms were proposed for the grafting of insoluble lignin and the activation of cotton cellulose fibers.

References

[1] H. K. Yasuda, Plasma polymerization and plasma interactions with polymeric materials, John Wiley and Sons, Ed., New York (1990).

[2] J. R. Roth, Industrial Plasma Engineering, vol. 2. Applications to Nonthermal Plasma Processing, IOP (2001).

[3] F. Denes, R. A. Young, M. Sarmadi, Surface functionalization of polymers under cold plasma conditions – a mechanistic approach, J. Photopolymer Sci. Technol. **10**, 91-112 (1997).

[4] Encyclopedia of Polymer Science and Engineering, John Wiley & Sons, Wiley Interscience Publishing, vol **8**, 795-852 (2003).

[5] C-L Chen, Lignins: occurrence in woody tissues, isolation, reactions and structure, in Wood Structure and Composition, M. Lewin, I.S. Goldstein Eds., Marcel Dekker Inc., New York, 183-261 (1991).

[6] J. J. Meister, Modifications of lignin, J. Macromol. Sci. C42, 2, 235-289 (2002).

[7] J. D. Gargulak, S. E. Lebo, Commercial use of lignin-based materials, in Lignin. Historical, Biological and Materials, Perspectives, W. G. Glasser, R. A. Northay, T. P. Schultz, ACS Symposium Series 742,Am.Chem. soc., Washington, 2001, pg 304-320.

[8] T. Q. Hu, Chemical Modification, Properties and Usage of Lignin, Kluwer Academic/Plenum Publishers, New York, 2002.

[9] R. Mahlberg, H. E. M. Niemi, F. S. Denes, R. M. Rowell, Application of AFM on the adhesion studies of oxygen-plasma-treated polypropylene and lignocellulosics, Langmuir, **15**, 2985-2991 (1999).

[10] C. I. Simionescu, G. Cazacu, M. M. Macoveanu, M. Totolin, Gh. Rozmarin, Chlorination and chloromethylation of cellolignine under the action of radiofrequency electrical discharges, Cell. Chem. Technol., **17**, 487-493 (1983).

[11] C. I. Simionescu, F. Denes, M. M. Macoveanu, G. Cazacu, M. Totolin, Fl. Popescu, S. Percec, Grafting of rayon with phosphorous-containing nonvolatile monomers to obtain flame-retardants fibres and fabrics, Cell. Chem. Technol. **13**, 463-475 (1979).

---

*Corresponding author: gcazacu@icmpp.ro