Synthesis of Novel Lignin-based Composite Materials Using Cold-Plasma Technique

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Lignin is a renewable raw material and it represents the third largest source of organic matter in the plant kingdom. It is estimated that only a couple of percent of available lignin are recovered and used in processes other than fuel technologies. Conventional research approaches applied for the modification of lignin have not resulted in the development of commercial technologies due to the inert, three-dimensional network structure of lignin, and to the elaborate, and expensive wet chemistry modification procedures. Non-equilibrium plasma chemistry technologies offer an alternative and efficient way for surface-functionalization of lignin particles. The cold-plasma (non-equilibrium) state denotes a partly ionized gas composed of electrons, ions of either polarity, gaseous atoms and molecules in the ground and any higher state, atoms and charged and neutral molecular fragments and light quanta. The energy levels of plasma species are comparable with the bond energies of organic molecules, including those containing main group elements, and as a consequence all chemical structures can conveniently be altered in the gas phase or in the surface layers of condensed materials by controlling the energy levels of plasma species [1- 4].

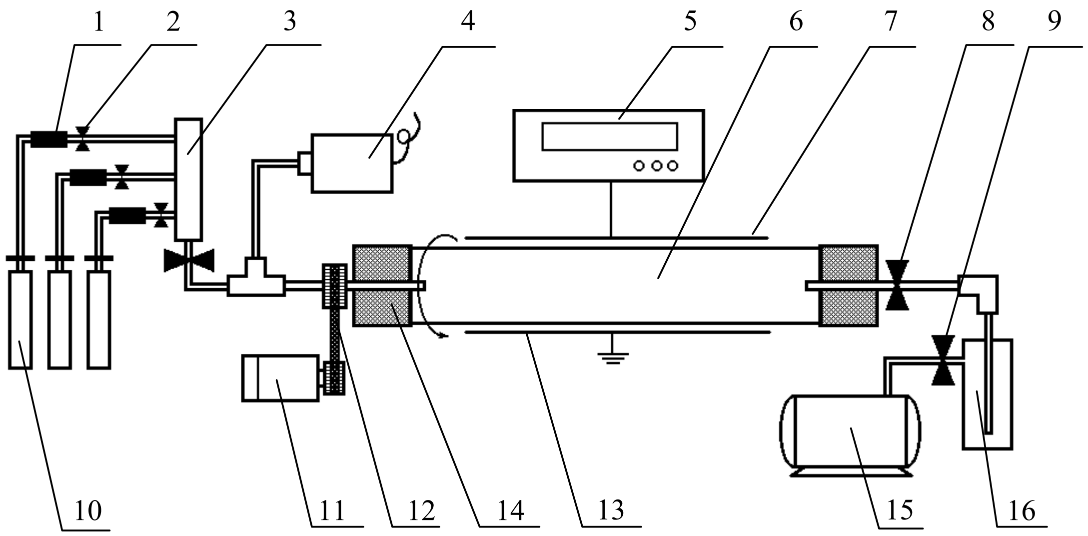

Figure 1. Rotating plasma reactor: 1—flow meters; 2—needle valves; 3—mixing chamber; 4—MKS vacuum gauge; 5—plasma power; 6—Pyrex glass chamber; 7—upper electrode; 8, 9—valves; 10—metallic reservoirs; 11—electric motor; 12—coupling belt; 13—lower electrode; 14—ferrofluid sealing; 15—nitrogen trap; 16—vacuum pump.

In this contribution plasma modification of Indulin lignin is described, and polyethylene glycol-, diamines- and epichlorohydrin-mediated composite material preparations are evaluated. All plasma modification reactions were carried out in a capacitively coupled 13.56 MHz discharge camber (Figure 1).

Argon-plasma-created free radical sites and –CH(O) functionalities were implanted onto lignin particle surfaces. Formaldehyde was generated from controlled, thermal decompo-sition of paraformaldehyde. Plasma-functionalized particulate lignin materials were grafted *in situ* and *ex situ* conditions using polyethylene glycol, ethylene diamine and epichlorohydrin. A hot-press technique was employed for the preparation of composite test samples.

The chemical nature of the surface-modified composite materials was evaluated using survey and high resolution ESCA and attenuated total reflectance Fourier transform IR spectroscopy (ATR-FTIR). Surface characteristics of the test sample coupons were investigated by scanning electron microscopy, atomic force microscopy and contact angle measurements. The presence of aldehyde functionalities were demonstrated using chemical derivatization techniques followed by X-ray photoelectron spectroscopy (ESCA) evaluations. Silver was deposited to the plasma-modified lignin particles according to the Tollen's reaction, and pentafluorphenylhydrazine was also used for the identification of –CH(O) groups. Potential application of RF plasma technology is discussed.

References

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