

Synthesis of Cross-Linked Humic Substances Using Phenol-Formaldehyde Polycondensation

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Keywords: humic substances, chemical modification, phenol-formaldehyde condensation, crosslinking

1. INTRODUCTION

Cross-linking is a perspective tool for synthesis of humic materials with higher molecular weight and lower solubility needed for their using as humic sorbents. The promising direction for controlled cross-linking of humics is curing of humic phenol-formaldehyde copolymers. By means of phenol-formaldehyde condensation, additional phenolic and quinonoid moieties can be incorporated into humic backbone. The former provide for complexing properties of humic materials, the latter for their redox-activity. Hence, cured humic sorbents can possess enhanced detoxifying ability with respect to heavy metals as well as higher reducing capacity with respect to redox-sensitive metals. The goal of this research was to synthesize cross-linked humic materials using phenol-formaldehyde condensation.

2. MATERIALS AND METHODS

Parent humic material: Humic acids of leonardite (CHA) used for further modifications were isolated from commercially available potassium humate (Powhumus) produced by Humintech Ltd, Germany.

Synthesis of humic novolacs: Formaldehyde condensation between mono- and dihydroxybenzenes and humic material under conditions of producing novolac resins was conducted (acidic catalysis) following (1). In case of phenol-

humic condensation, the amounts of phenol were 50, 100 and 250 mg per 1 g of CHP (ca. 5 mmol of acidic groups). In case of phenol/hydroquinone condensation with humic material, the amounts of monomers were 100 and 250 mg (molar ratio phenol : hydroquinone was 1:1, respectively, per 1 g of CHA).

Cross-linking of humic novolacs: A weight of humic novolac was mixed with paraformaldehyde or hexamethylenetetramine at the ratio of 1 mole Ar-OH per 0.6 mole of $-\text{CH}_2-$ moieties. The mixture of solid reagents was placed into an drying oven for 30 min at $t = 110^\circ\text{C}$.

Synthesis of humic resoles: Formaldehyde condensation between phenol and humic material under conditions of producing resole resins (alkaline catalysis) was conducted following (2). The amounts of phenol were 50, 100 and 250 mg per 1 g of CHA (ca. 5 mmol of acidic groups).

Cross-linking of humic resoles: A weight of the humic resoles were placed into an drying oven for 2,5 hours at $t = 130^\circ\text{C}$.

To determine molecular size of synthesized humic derivatives, ultrafiltration was used.

Total acidity of humic derivatives was determined using barita technique as described elsewhere (3).

Reducing capacities of humic materials were determined using ferricyanide as oxidizing agent as described in (4).

3. RESULTS AND DISCUSSION

Synthesized preparations were investigated using elemental analysis, functional group analysis, ultrafiltration, IR and ^{13}C NMR spectroscopy. Typical ^{13}C NMR spectra are presented in Figure 1. It can be seen that spectra of the derivatives are characterized with the presence of sharp spikes that are absent in the spectrum of the parent material. Peaks at 60 to 70 ppm in the phenol-humic resole spectrum can be assigned to methylol groups and oxymethylene bridges. Peaks at 120 - 130 ppm in the phenolic copolymer spectra indicate the presence of aromatic carbon substituted with methylene groups. Sharp peaks present in the spectra of hydroquinone copolymers can be assigned to paraformaldehyde and hexamethylenetetramine - admixtures of these crosslinking agents in the final products.

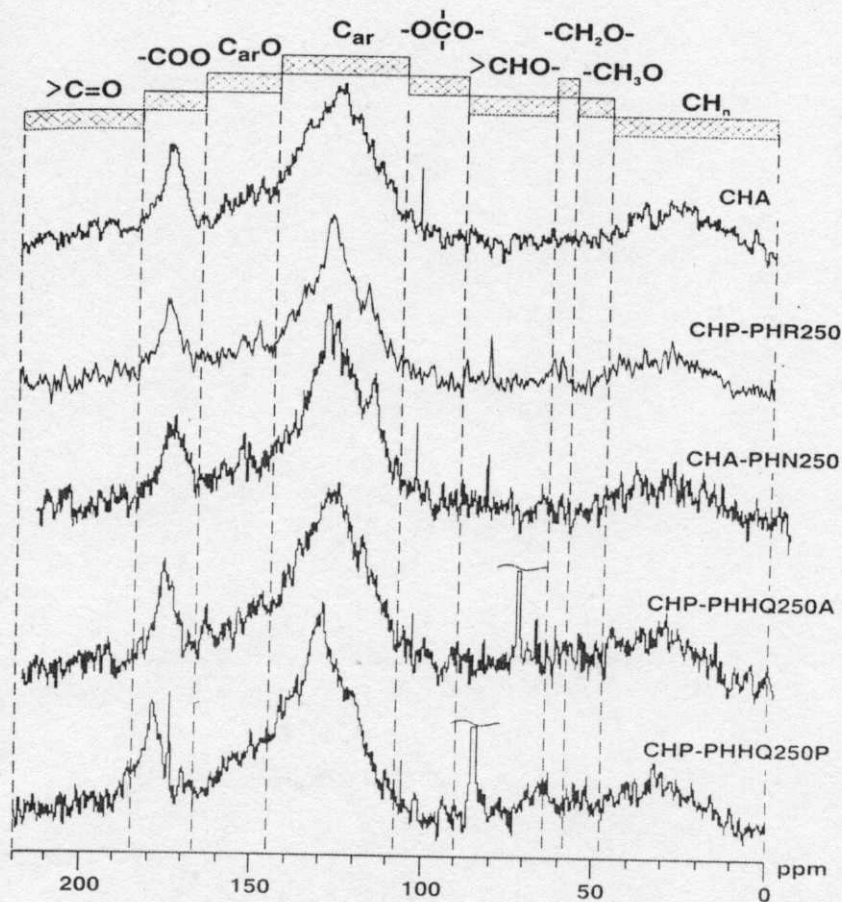


Figure 1: ^{13}C NMR spectra of humic derivatives. CHA – parent material, CHP-PHR250 – phenol-humic resole, CHP-PHN250 – phenol-humic novolac, CHP-PHHQ250A – phenol-hydroquinone-humic novolac crosslinked by hexamethylenetetramine, CHP-PHHQ250P – phenol-hydroquinone-humic novolac crosslinked by paraformaldehyde.

Results on molecular weight distribution of crosslinked humic resols and novolacs were obtained using ultrafiltration. Ultrafiltration data showed that copolycondensation between humic substances and hydroxybenzenes resulted in formation of higher molecular weight polymeric fraction (>300 kD); its content has increased up to 25 % during crosslinking.

It should be noted that in case of crosslinked humic novolacs and resols, insoluble fraction was detected with size > 0.45 μm . The contribution of this fraction into humic copolymers crosslinked by hexamethylenetetramine

increased along with an increase in monomer : CHA ratio. At the same time, this dependence was not observed in case of paraform crosslinking. Titration data indicated that content of phenolic group of novolacs and resoles increased with increasing amount of phenol used in reaction and it was about half as much again greater than that of parent material. At the same time content of phenolic group of all crosslinked copolymers were lower than that of corresponding non-crosslinked copolymers. The greatest decrease in phenolic content was observed for thermally cured copolymers. Reducing capacity of hydroquinone copolymers changed in the same manner. It can be explained by sterical hindrances appeared in more crosslinked structures that complicate reactions with phenolic hydroxyls.

4. CONCLUSIONS

Phenol-formaldehyde condensation was proposed as a perspective tool for synthesis of cross-linked humic substances. It was shown that phenol-formaldehyde condensation yielded humic derivatives with higher content of phenolic moieties, higher molecular weight and less soluble in water.

ACKNOWLEDGEMENTS

The research was supported by the International Science and Technology Center (project KR-964) and NATO (CLG #°980508).

REFERENCES

- (1) Perminova, I. V. et al.: Design of quinonoid-enriched humic materials with enhanced redox properties. *Environ. Sci. Technol.* 39(21), 8518-8524 (2005).
- (2) Lee Y.-K. et al.: Activation energy and curing behavior of resol- and novolac-type phenolic resins by differential scanning calorimetry and thermogravimetric analysis. *J. Appl. Polym. Sci.* 89, 2589-2596 (2003).
- (3) Swift, R. S.: Organic matter characterization in methods of soil analysis. Part 3, Chemical methods. In *Methods of Soil Analysis*, 1036-1041 (1996).
- (4) Matthiessen, A.: Determining the redox capacity of humic substances. *Vom Wasser* 84, 229-235 (1995).