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► To cite this version:

Antonio M Borrero-López, Jimena Castro-Gutiérrez, A. Celzard, Vanessa Fierro. Coal tar residues as precursors of hypercrosslinked polymers: using mechanosynthesis as a green synthesis protocol. GEP-SLAP 2022, Grupo Especializado de Polímeros, May 2022, San Sebastián, Spain. hal-03873426

HAL Id: hal-03873426

<https://hal.univ-lorraine.fr/hal-03873426>

Submitted on 30 Oct 2023

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Coal tar residues as precursors of hypercrosslinked polymers: using mechanosynthesis as a green synthesis protocol

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Introduction

Hypercrosslinked polymers (HCPs) are defined as a new type of intricate polymers, where a high level of entanglement is achieved. They comprise pores (usually in the nano/mesoporosity range) and stable rigid materials, and have proven useful in several applications, such as chromatography, gas adsorption, sensing, catalysis, drug delivery, heavy metal ions and hazardous dyes removal, etc. [1]. However, they are usually synthesized from non-renewable resources and thus from environmentally unfriendly precursors, such as benzene and its derivatives, and using time-consuming and hazardous solvent-based Friedel-Crafts reactions. In this sense, there has recently been renewed interest in an older, greener and faster technique, mechanosynthesis (MS), which allows the synthesis of similar products in much shorter timescales (from days to minutes), and eliminates the need for hazardous solvents. Therefore, by studying the influence on the final product of various MS parameters (mill and ball materials, size and number of balls, ball mill volume, rotation speed or vibration frequency, reaction time, crosslinker / monomer and catalyst / monomer ratios), good yields and highly porous HCPs can be obtained [2]. However, generally hazardous precursors are still used, which limits HCP development [1,2]. Thus, in this study, residues from the processing of coal tar products are used, which also allows their valorisation. These HCPs are considered to be effective

agents for the removal of contaminants from water.

Experimental

Materials

For the formulation of HCPs based on Friedel-Crafts reaction using MS, a crosslinker, a catalyst and a precursor are needed. Thus, formaldehyde dimethylacetal (FDA), iron chloride and different coal tar-derived fractions (creosote, phenolic oil, wash oil and chrysene oil, supplied by Bilbaina de Alquitrane S.A. (Bizkaia, Spain)) were used as crosslinker, catalyst and precursors, respectively. Benzene was used as a model molecule to serve as a precursor and the results obtained with benzene were compared with those obtained with coal tar-derived fractions. The MS was monitored in a 250 mL capacity stainless-steel bowl filled with 50 balls of 10 mm diameter.

Preparation of HCPs

The procedure for the preparation of HCPs by MS was very simple and straightforward. Under an inert atmosphere, the precursor, catalyst and crosslinker were added simultaneously in different proportions into the MS bowl, also containing the 50 balls. Then, the bowl was stirred at 500 rpm for different periods of time using a PM 100 planetary ball-milling machine (Retsch). The resultant material was thoroughly washed to eliminate the remaining FeCl_3 and unreacted precursors and crosslinker. The washing was first performed with ethanol and methanol several times, followed by a subsequent Soxhlet extraction using a toluene /

ethanol solution (in a 32/68 w/w ratio) solution for 24 h [2]. Then, the samples were dried at 80°C under vacuum for 24 h to remove the remaining solvent.

Characterization of HCPs

TGA/MS characterization was performed using a STA 449F3 Jupiter microbalance (Netzsch) coupled to a QMS 403 D mass spectrometer. The sample was heated under inert atmosphere, N₂, to 900°C at a rate of 10°C/min, then held at 900°C for 30 min.

N₂ adsorption/desorption isotherms at -196°C were performed using a Belsorp Max II (Microtrac), in the 10⁻⁷-1 relative pressure range. The samples were previously outgassed at 60°C under secondary vacuum. BET area (A_{BET}) and pore volume were calculated from these isotherms.

Results and Discussion

Benzene was selected as the model aromatic molecule to obtain aromatic-based HCPs. Reaction times of 3 to 15 min were tested, maintaining the other MS conditions constant and choosing a precursor/FeCl₃/FDA molar ratio of 1/6/2. As can be observed in Figure 1, close A_{BET} values of 515-590 m²/g were obtained using benzene regardless of reaction time. Thus, different creosote-based HCPs were also synthesized to check the influence of reaction time. Reaction times of 5, 10 and 15 min were tested, using a similar precursor/FeCl₃/FDA molar ratio as used with benzene. The determined A_{BET} is also plotted in Figure 1, where a significant reduction compared to the benzene-based HCP is clearly visible. The maximum A_{BET} , 170 m²/g, was obtained at 10 min and very close A_{BET} were obtained at 5 and 15 min, as found with the benzene-based formulations.

Due to the subtle differences when varying the reaction time, a 5 min reaction time was selected to synthesize the HCPs with the remaining precursors, namely: phenolic oil, wash oil and chrysene oil. The TGA results of these HCPs are shown in Figure 2. As it can be observed, each precursor exhibits a different behaviour, creosote being the one with the lowest degradation onset temperature, around 140°C. The HCP based on

phenolic oil starts its degradation around 210°C, and the others around 230°C. It is also worth mentioning that, even reaching 900°C, a remarkable pyrolysis yield was obtained, ranging from 60% for the phenolic oil-based HCP to the 72% for the chrysene oil-based HCP.

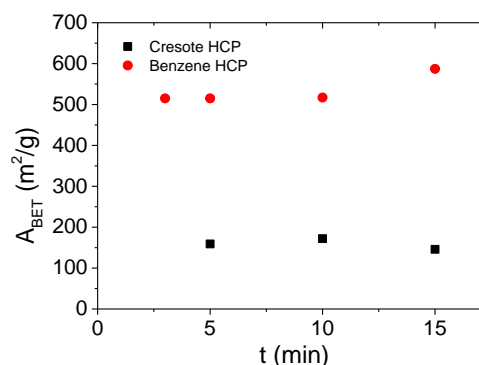


Figure 1. A_{BET} determined from N₂ adsorption/desorption isotherms on HCPs prepared at different reaction times from benzene and creosote.

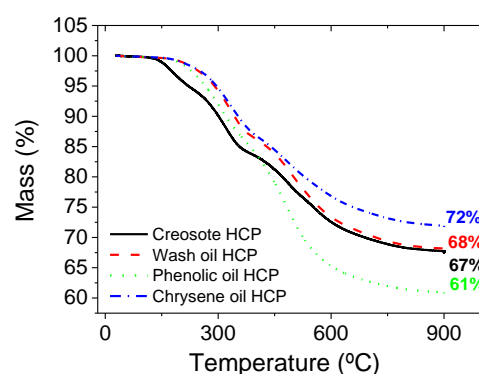


Figure 2. Results of TGA under N₂ for HCP derived from different coal tar residues.

These HCPs will be used for the adsorption of pollutants in aqueous phase, a study that is currently in progress.

Acknowledgements

This work is part of the UCGWATERplus research project sponsored by the Research Fund for Coal and Steel (2020). A.M.B.-L. also thanks the Margarita Salas (SOL-RPU-59) grant received.

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