

PREPARATION AND CARBONIZATION OF POROUS SARAN CARBON MONOLITHS USING HIGH INTERNAL PHASE EMULSION TEMPLATING

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Introduction

Porous polymeric structures formed by polymerizing the monomer-containing continuous phase of a high internal phase emulsion (HIPE) have been called polyHIPEs. They can be used as precursors for carbons that maintain the morphology of the polymer, although they undergo dimensional shrinkage as well as weight loss on carbonization. Following formation of a stable emulsion, polymerization of the continuous phase yields a porous, monolithic polymer with interconnected voids throughout the structure. The emulsions can be cast to produce monoliths of a variety of shapes. The synthesis, control of macroporous structure, and a variety of actual and potential applications of have been reviewed [1, 2, 3]. Carbonized polyHIPEs that have been reported include those derived from methacrylonitrile-divinylbenzene, resorcinol-formaldehyde, styrene-divinylbenzene and 4-vinylbenzyl chloride polymers [4]. Poly(vinylidene chloride) (PVDC) and Saran copolymers are of interest as candidate polymers for carbonized polyHIPEs due to the properties of the derived carbons. Carbons prepared from poly(vinylidene chloride) and similar Saran copolymers have high adsorptive capacity with surface area concentrated in micropores. Carbonization of solid or compressed polymer pellets does not yield material with suitable characteristics when high fluid permeability and low flow resistance are important. High internal phase emulsions as templates for these carbon precursors is a possible synthetic route to a highly macroporous, interconnected structure. Synthesis of PVDC from high internal phase emulsions is problematic as the monomer's boiling point is below the typical useful temperatures of thermal polymerization initiators. While stable emulsions using vinylidene chloride can be made, they separate when heated to initiate polymerization. This paper reports the synthesis and characterization of polyHIPEs by addition of pre-polymerized material to an emulsion of more readily polymerized monomer. Styrene-divinylbenzene was used to form emulsions and the pre-polymerized material was Saran copolymer. The polymers were carbonized under nitrogen to produce carbon monoliths with an open, interconnected macroporous structure and the microporous character inherent in carbon derived from Saran polymer [5, 6].

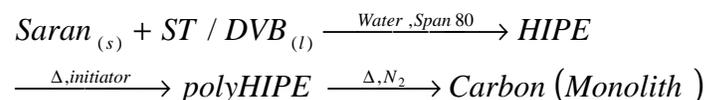
Experimental

Emulsions and polyHIPEs were made using styrene (ST) and divinylbenzene (DVB) as cross-linker. The polymerization initiator was potassium persulfate, and sorbitan monooleate (Span 80) was used as surfactant to form stable emulsions. Dow Chemical Saran 506, a copolymer of vinylidene chloride

and vinyl chloride in the form of micronized powder 15 to 25 μm was added to the emulsions prior to polymerization. Polymerized monolith samples were carbonized under nitrogen at 700 $^{\circ}\text{C}$. BET surface area of samples was measured by nitrogen adsorption isotherms at 77 K [7]. Macropore structure was analyzed using SEM and mercury intrusion porosimetry.

Results and Discussion

Micronized polymer powders of Saran copolymer were used to modify styrene-divinylbenzene polyHIPEs.



Emulsions could be formed successfully at all added polymer fractions attempted up to 0.67 by weight by wetting the polymer powder with the styrene-divinylbenzene monomer mixture prior to forming the emulsion. Following polymerization of the emulsion, a typical porous structure resulted, but with the added polymer embedded in the structure (Figure 1a).

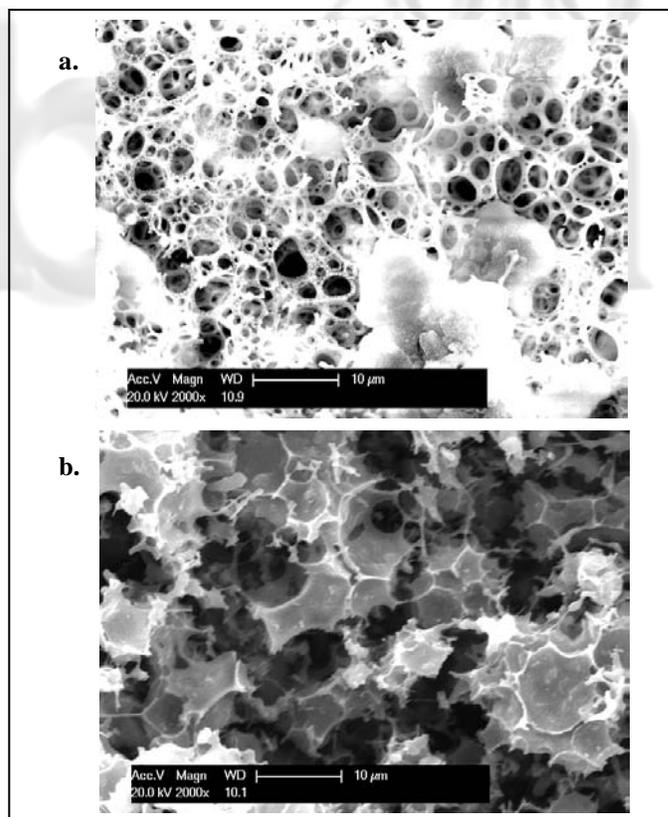


Figure 1. a. SEM image of uncarbonized polyHIPE with embedded polymer particles. b. Carbonized monolith.

The addition of polymer powder caused a decrease in the window diameter of the polyHIPEs and a decrease in total void volume as fraction of added Saran polymer increased. The added polymer in all cases stabilized the polyHIPE for carbonization (Figure 1b), while a ST-DVB polyHIPE without polymer would melt and fuse at carbonization temperatures, thereby losing the structure of the precursor polymer monolith. The mechanism of stabilization of the morphology may involve the melt-flow of Saran polymer at low temperatures in the carbonization process, thereby stabilizing the ST-DVB structure. The combination of weight loss and dimensional shrinkage on carbonization resulted in relatively little change in density compared to the precursor monolith. A large increase in surface area resulted from carbonization, typically from 5 m²/gram for the uncarbonized polyHIPE to 400-500 m²/gram when carbonized. Greater than 80% of this surface area was concentrated in micropores, with a micropore volume of up to 0.2 cm³/gram. Although the specific surface area of carbonized Saran would not be expected to change with amount added to the polyHIPE, the relative amounts of polystyrene and Saran polymer will have an effect on a volume basis.

Table 1. Carbonized polyHIPE Monoliths

Added Saran	Carbonized Density	BET Surface Area	Micropore Surface Area	Micropore Volume
Weight Fraction	grams/cm ³ (std. dev.)	m ² /gram (std. dev.)	m ² /gram (std. dev.)	cm ³ /gram (std. dev.)
0.40	0.127 (0.051)	484 (53)	422 (58)	0.186 (0.014)
0.58	0.183 (0.046)	480 (23)	418 (9)	0.195 (0.011)
0.67	0.204 (0.009)	430 (44)	406 (-)	0.200 (-)

The macropores of the polyHIPEs and the derived carbon monoliths showed a narrow distribution of window diameters. Carbonization of the polymer monoliths caused an increase in window diameter (Figure 2). The diameters will depend on conditions of synthesis of the polyHIPE, in this case representative window diameters ranged from 1 to 10 μm. The macropore volumes of the carbon monoliths were in the range of 3.5 to 4.0 cm³/gram as measured by mercury intrusion porosimetry.

Conclusions

Micronized polymer powders of Saran (vinylidene chloride-vinyl chloride) copolymer were used to modify styrene-divinylbenzene polyHIPEs. Emulsions could be formed successfully and polymerized to form a modified polyHIPE with embedded polymer particles. This increased the density of the polyHIPE compared to unmodified ST-DVB polyHIPEs

made using the same synthetic conditions. The added polymer had the additional benefit of stabilizing the polyHIPE for thermal degradation to carbons that retained the morphology of the precursor polymer. The addition of micronized powders to monomer emulsions is a useful route to preparation of macroporous polymer monoliths, followed by pyrolysis under nitrogen to yield carbon monoliths with interconnected, macroporous structures and microporous character.

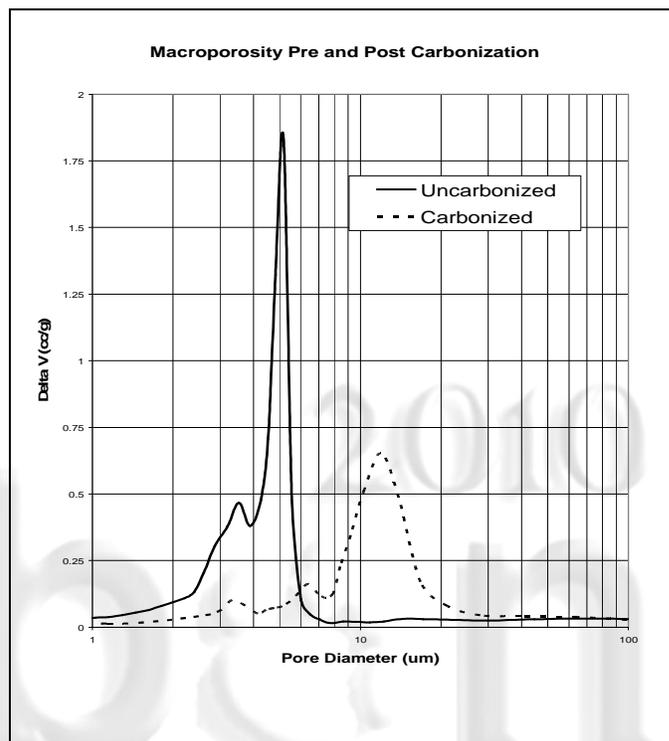


Figure 2. Macropore size distribution of a monolith before and after carbonization. Added polymer weight fraction 0.58.

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