Materials and Design 79 (2015) 115–126

Contents lists available at ScienceDirect

Materials and Design

journal homepage: www.elsevier.com/locate/matdes

Tannin-based monoliths from emulsion-templating

A. Szczurek [a], A. Martinez de Yuso [a], V. Fierro [a], A. Pizzi [b,c], A. Celzard [a,*]

[a] Institut Jean Lamour, UMR CNRS – Université de Lorraine n°7198, ENSTIB, 27 rue Philippe Séguin, CS 60036, 88026 Epinal Cedex, France
[b] LERMAB, EA Université de Lorraine n°4370, ENSTIB, 27 rue Philippe Séguin, CS 60036, 88026 Epinal Cedex 9, France
[c] King Abdulaziz University, Jeddah, Saudi Arabia

ARTICLE INFO

Article history:
Received 4 February 2015
Revised 4 April 2015
Accepted 11 April 2015
Available online 24 April 2015

Keywords:
Tannin
Porosity
PolyHIPE
Thermal conductivity
Mechanical properties

ABSTRACT

Highly porous monoliths prepared by emulsion-templating, frequently called polymerised High Internal Phase Emulsions (polyHIPEs) in the literature, were prepared from "green" precursors such as Mimosa bark extract, sunflower oil and ethoxylated castor oil. Various oil fractions, ranging from 43 to 80 vol.%, were used and shown to have a dramatic impact on the resultant porous structure. A critical oil fraction around 70 vol.% was found to exist, close to the theoretical values of 64% and 74% for random and compact sphere packing, respectively, at which the properties of both emulsions and derived porous monoliths changed. Such change of behaviour was observed by many different techniques such as viscosity, electron microscopy, mercury intrusion, and mechanical studies. We show and explain why this critical oil fraction is the one leading to the strongest and most homogeneous porous monoliths.

1. Introduction

Porous monoliths prepared by emulsion-templating of polymers are remarkable materials having many potential applications in chemical engineering for gas adsorption and separation [1–4] or for catalysis [5–11], and in biomedical sciences as vehicle for drug delivery [12] or as scaffold for tissue engineering [13–16]. Such materials indeed present a highly developed, fully interconnected, porosity, obtained by polymerising the continuous phase of high internal phase emulsions (HIPEs), hence their name: polyHIPEs. PolyHIPEs were first developed and patented by Unilever [17]. Such materials are based on the preparation of a mixture of two immiscible phases, e.g. water and oil, in which the internal phase has a high volume fraction, typically higher than 74%. The latter value indeed corresponds to the compacity of a FCC or HCC packing of uniform spheres [18]. Emulsions with high concentration of dispersed phase can easily undergo a conversion from W/O to O/W and vice versa. Therefore, using of surfactant is required for preventing this phenomenon, but also for maintaining the structure of the emulsion before it is irreversibly converted into a hard material.

Most studies reported in the literature focused on polyHIPEs based on water in oil concentrated emulsions. In these cases, hydrophobic monomers were used as building blocks of the continuous phase, thereby leading to the typical skeletal structure of foam, whereas water was the dispersed phase, whose droplets produced the porosity. In such W/O emulsions, the styrene–divinylbenzene system was by far the most representative and investigated one for preparing solid polyHIPEs. For the latter, polymerisation of styrene monomer took place in oil phase in the presence of divinylbenzene used as a crosslinker, and the water phase was used as porogen and was removed after complete polymerisation. The resultant polyHIPEs presented outstanding porosity with uniform pore sizes, wherein control of pore size was easily made through some changes in the experimental conditions [18–20].

The second, O/W type, emulsion is less common in polyHIPEs' synthesis. However, it leads to similar materials having comparable porosities and pore sizes as those obtained from W/O emulsions [15,21–26]. In this case, an aqueous solution of polymer is prepared and acts as the continuous phase, whereas oil is the porogen and is subsequently leached out by extraction with a suitable solvent. Most of polymer precursors used this way are based of synthetic monomers which lead to highly porous monoliths presenting uniform and well-controlled porosity, and are characterised by good mechanical resistance. However, most of them are derived from toxic and non-renewable chemistry. Due to this, attempts have been successfully made for preparing polyHIPEs based on lignin [27–29], but the preparation of the latter was based on highly alkaline black liquors crosslinked by epichlorhydrin or cyanuric chloride, so that the advantage of their plant origin is not so obvious.

The most environment-friendly and "green" precursors, presenting similar reactivity as synthetic phenolic molecules, are

* Corresponding author.
E-mail address: alain.celzard@univ-lorraine.fr (A. Celzard).

http://dx.doi.org/10.1016/j.matdes.2015.04.020
0261-3069/

condensed (flavonoid) tannins. They can undergo some of the typical reactions of phenol such as polycondensation reaction with formaldehyde but also with other far less toxic and volatile aldehydes, under slightly acidic or alkaline conditions. Condensed tannins are based on nontoxic flavonoids extracted from plants. Mimosa (*Acacia mearnsii*, De Wild) tannin extracts, used in the present work, are mainly based on prorobinetinidin, an oligomer whose structural unit is based on resorcinol A-ring and pyrogallol B-ring, see Fig. 1(a). Such compound thus contains 5 hydroxyl groups. Prorobinetinidin represents about 70% of the total content of tannin in the Mimosa bark extract. The second most common component of condensed mimosa tannin is profisetinidin, based on resorcinol A-ring and catechol B-ring, see Fig. 1(b), and represents 25% of Mimosa bark extract. Other components are non-tannins, which consist of carbohydrates, hydrocolloid gums, and small fractions of amino and imino acids. The oligomers are constituted by flavonoid repeating units as shown in Fig. 1(c), mostly linked C4–C6 or C4–C8 to each other.

The addition reaction of formaldehyde on tannin produces hydroxymethyl groups mainly on C8 or C6 sites [30]. As a consequence of crosslinking with aldehydes, polyflavonoid tannins give resins constituting the backbone of various kinds of porous monoliths, such as gels [31,32], foams [33–37] and, as shown here, polyHIPEs. Most of these organic materials are characterised by porosities within the range 80–95%. Their characteristics strongly differ depending on the way the materials were prepared. For instance, tannin gels are mainly micro/mesoporous and have high surface area within the range 400–1000 $m^2 g^{-1}$ [31,32], while foams present a typical macroporous, cellular, structure [33]. These low-density materials present good mechanical properties, are extremely resistant to fire [38 and refs. therein] and have excellent thermally insulating properties.

In the present work, the physical properties of tannin-based, emulsion-templated, porous monoliths – alternatives to tannin-based classical rigid foams [39], are described. Their carbonaceous counterparts were already investigated elsewhere [22,23], but this is first time that the properties of the organic materials from which they can be derived are detailed. Organic and carbon materials indeed obviously present different mechanical, electrical, thermal but also structural and textural properties, as carbonisation induces the development of additional porosity and surface area as well as a significant volume shrinkage. Besides, organic materials present a surface that is highly rich in hydroxyls groups, as suggested by Fig. 1(c), through which functionalization by various moieties, including enzymes, can be carried out for catalysing a number of specific reactions [21]. The thorough investigation of

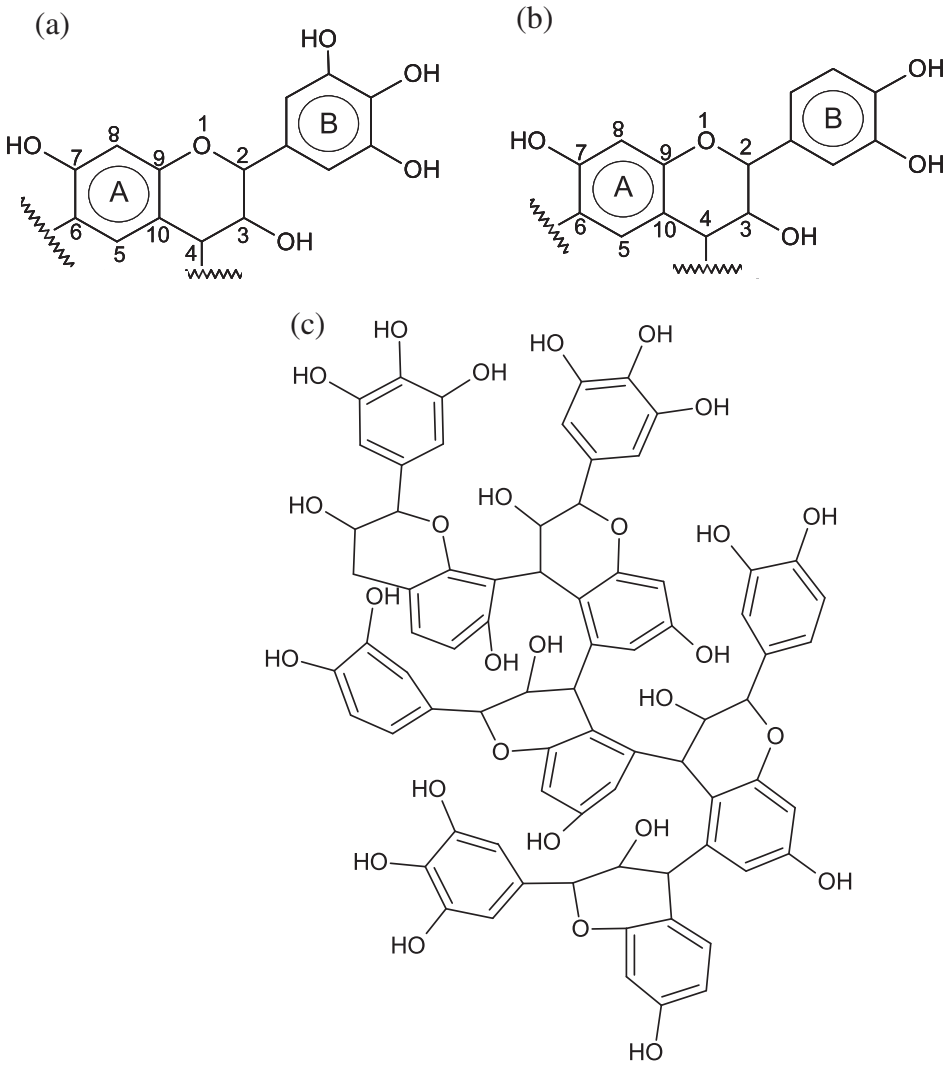

Fig. 1. Main compounds in Mimosa bark extract, used for producing emulsion-templated, tannin-based, porous monoliths: (a) prorobinetinidin unit; (b) profisetinidin unit; (c) possible mimosa tannin oligomer based on 5 flavonoid units.