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Water expandable polystyrene containing cellulose nanofibrils: Expansion behavior and morphology

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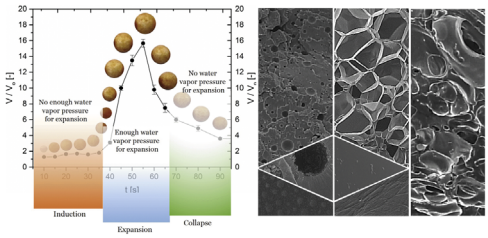
HIGHLIGHTS

- Water expandable polystyrene bead was synthesized using cellulose nanofibrils as w/o Pickering emulsion polymerization.
- The water content was investigated over months and discussed.
- The expansion behavior of beads was investigated over months and discussed.
- The morphology of expanded beads was investigated and discussed.

GRAPHICAL ABSTRACT



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ABSTRACT

Here, we reported a new type of water expandable polystyrene (WEPS) beads containing cellulose nanofibrils (CNFs). This expansible material, called CNFWEPS, showed the highest expansion ratio (~16) for the as-synthesized beads and ~8 after 4.5 months, which has never been reported in the literature. Expandable beads containing 9–13 wt% of the well-dispersed water were synthesized through Pickering emulsion polymerization of styrene in the presence of CNF. During the polymerization, CNFs rearrange and create nanospheres which entrap water inside polystyrene beads. Morphological investigations along with thermogravimetric analysis showed that the entrapped water is either discrete water droplets of 9–10 μm in diameter or bound water with a strong adsorption to the hydrophilic nanoparticles inside the beads. Importantly, the bound water could be preserved several months after synthesis and therefore prolong the shelf-life of the CNFWEPS beads. The analysis of the expansion kinetics of the CNFWEPS beads revealed three-regime behavior with strong temperature dependency. The highest expansion ratio was obtained at 135 °C for the sample containing 0.2 wt% of CNF. Overall, apart from stabilization of water in the beads, the vital role of CNF unveiled to be reinforcing the foam structure and inhibiting the cell wall rupture by increasing melt strength of the matrix during expansion.

1. Introduction

Water expandable polystyrene (WEPS) is a new generation of expanded polystyrenes, in which instead of volatile organic compounds (VOC) e.g. pentane, water is used as blowing agent. As a promising eco-friendly product and despite of several novel and creative developments in the synthesis methods (Crevecoeur et al., 1999a, 1999b, 1999c; Pallay et al., 2000; Snijders et al., 2006; Shen

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et al., 2006; Amiri et al., 2009), however, WEPS is still far from commercialization. While, the density of commercial EPS grades is in the range of 15–35 kg m^{-3}, i.e. the expansion ratio of around 15–35. However, the best reported expansion ratio for WEPS is around 5–7, so far, which is lower than commercial EPS products. This is mainly due to low expandability of WEPS beads which in turn resulted from the inability of polystyrene (PS) matrix to preserve the blowing agent (water) during storage and expansion.

To cope with the problem of water loss during expansion and storage, recently, we have suggested a new synthesis route in which solid natural polymeric nanoparticles, e.g. cross-linked starch nanoparticles and cellulose nanofibrils (CNFs), were used to stabilize the water microdroplets inside the polystyrene beads (Nikfarjam et al., 2014, 2015a). Specifically, we exploited surfactant-free Pickering emulsion polymerization of styrene in water/oil/water (w/o/w) system to obtain expandable polystyrene beads. Depending on the synthesis condition and the formulation used, the as-synthesized beads contained 0–13 wt% well-dispersed water microdroplets (Nikfarjam et al., 2014, 2015a).

Comparing cross-linked starch nanoparticle (CSTN) (Nikfarjam et al., 2014) and CNF as water stabilizing agent, at the same content, the CNF can entrap much more water than CSTNs. For instance, in the presence of 3 wt% of CSTN, 12 wt% water was entrapped inside the beads, however only 0.8 wt% of CNF was able to stabilize the same amount of water (Nikfarjam et al., 2014, 2015a). The difference was ascribed to the different mechanism by which the CNF acts as the stabilizing agent (Nikfarjam et al., 2015a). This difference in water stabilization mechanism might lead to different morphology and expansion behavior in beads prepared by CNF. In our previous work, we investigated the expansion behavior of the water expandable polystyrene containing CSTN (Nikfarjam et al., 2015b). Here, we focus on the expansion characteristics of the CNFWEPS beads and explore the effect of CNF content and temperature on the kinetics of expansion and foam morphology. Furthermore, the effect of aging, i.e. ability of the beads to preserve the entrapped water during storage is investigated.

2. Experimental

2.1. CNFWEPS beads

The CNFWEPS samples containing different CNF content were prepared and characterized according to the procedures described in our previous report (Nikfarjam et al., 2015a). In brief, CNF was prepared using bleached soft Kraft pulp (2 wt%) by a SupperMassColloider (MKZA6-2, Masuko Sangyo Co., Ltd., Japan). Then, well dispersed CNFs in water, swelled overnight, was added to the partially polymerized styrene at 90 °C for 75 min under mechanical agitation and the sonicated for 90 s to obtain a so-called inverse emulsion. Degree of conversion of styrene was around 25% as determined by gravimetrical method. Subsequently, the obtained mixture was quickly suspended in water containing suspension stabilizer, hydroxyethyl cellulose in 1.2 wt% concentration, at 90 °C to complete polymerization and obtain spherical PS beads comprised water microdroplets (Fig. 1A and B) (Nikfarjam et al., 2015a). All samples were characterized for incorporated water content, water droplet number density and volume-weighted average water droplet diameter ($d_{4,3}$) (Table 1).

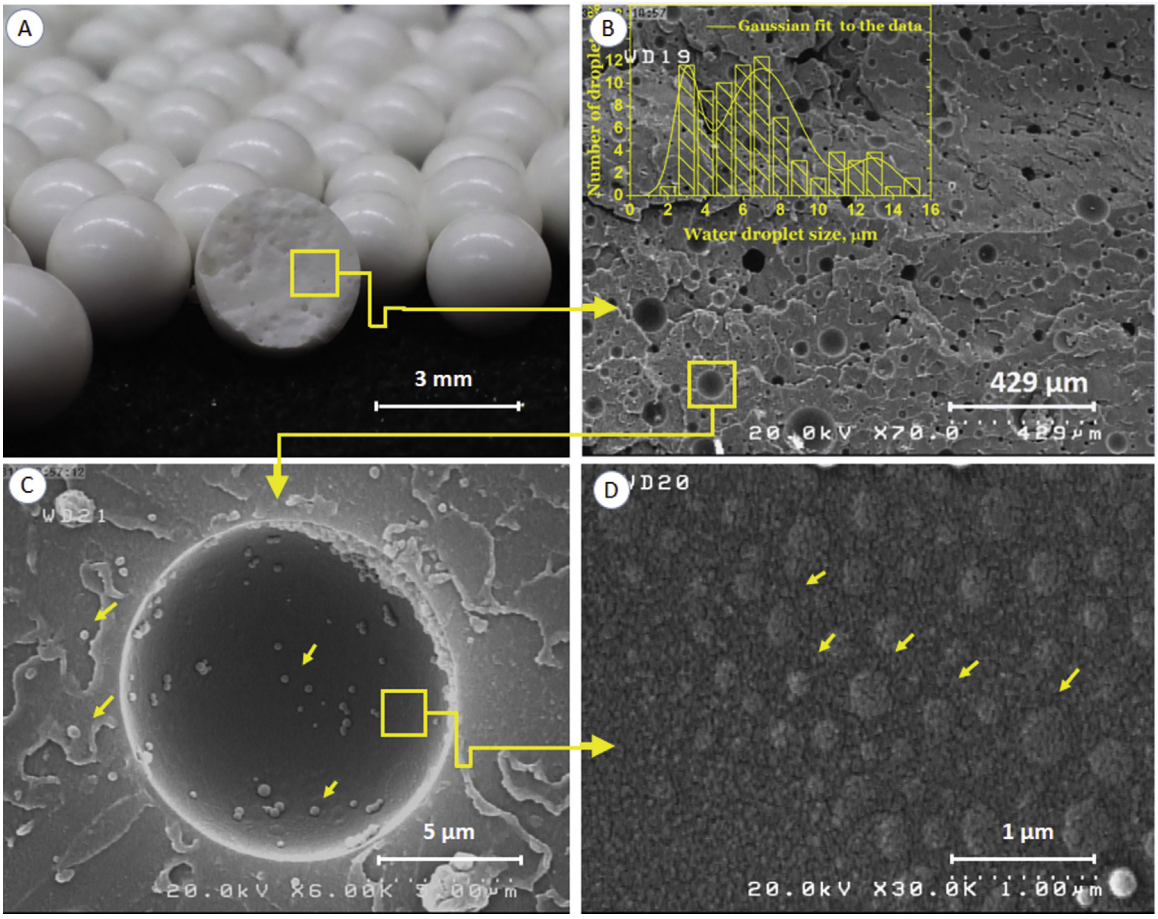

Fig. 1. Cross-section FE-SEM micrographs of the CNFWEPS compact beads, the CNF/PS nanospheres reside at the interface and physically stabilize the emulsion and some of them are encapsulated inside water droplets, in water phase. (A) Compact beads, (B) cross-section of a compact bead, (C) and (D) a water droplet site and interior wall of the droplet site at higher magnifications, respectively. (Fig. 1C and D were reprinted with permission from Nikfarjam et al., 2015b. Copyright 2015 Elsevier).