Chemical Engineering Journal 219 (2013) 254–261

Contents lists available at SciVerse ScienceDirect

Chemical Engineering Journal

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

Ultrasound assisted synthesis and characterization of poly(methyl methacrylate)/$CaCO_3$ nanocomposites

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HIGHLIGHTS

- Combined use of ultrasound and conventional chemical initiation improves final conversion.
- Combined technique offers smaller particle size and narrow size distribution.
- Composite and core–shell particles obtained explained by dual pathway mechanism.

ARTICLE INFO

Article history:
Received 3 September 2012
Received in revised form 31 October 2012
Accepted 5 January 2013
Available online 11 January 2013

Keywords:
Ultrasound
PMMA
$CaCO_3$
Nanocomposites
Emulsion polymerization

ABSTRACT

The combined effects of sonochemical and conventional chemical initiation on the emulsion polymerization of methyl methacrylate (MMA) and MMA–$CaCO_3$ systems have been studied. Combining ultrasound (US) and conventional initiation by potassium persulfate (KPS) for the MMA and MMA–$CaCO_3$ systems, helped increase the final conversion. An increase of 15% for the MMA only system (from 72% to 87%) and of 10% for the MMA–$CaCO_3$ system (from 76% to 86%) was observed as compared to initiation by KPS alone. Also, an increase of 18% (from 69% to 87%) and 20% (from 66% to 86%) for the MMA only and MMA–$CaCO_3$ systems, respectively was observed for the combined initiation as compared to initiation by US alone. Although all particles synthesized were in the size range of 60–130 nm, the excellent dispersion ability of ultrasound helped to obtain narrow size distribution and smaller average sizes in both the PMMA and PMMA–$CaCO_3$ systems. Possible mechanisms have been proposed for both the polymerization and the formation of poly-MMA–$CaCO_3$ composite and core–shell nanoparticles taking into account the results obtained by analyzing the synthesized materials.

1. Introduction

The chemical effects of ultrasound have been well-explained as the consequence of localized hot spots created during the collapse of cavitation bubble. The collapse of bubbles produces intense local heating (~5000 K) and high pressures (~1000 atm) with very short lifetimes and heating and cooling rates above 10^{10} K/s [1]. The different ways in which ultrasonic input can beneficially affect a chemical reaction have been discussed [2] and such beneficial effects have been used for (amongst other things) carrying out emulsion polymerization [3] of monomers like methyl methacrylate [4,5], butyl acrylate [6,7] and styrene [8–10].

The results from these studies have proven the efficacy of the use of ultrasound in emulsion polymerization. First, the physical effects, generated by the cavitation process, act to disperse approximately uniformly sized monomer droplets in the aqueous phase. The (primary) H and OH radicals created by the sonolytic decomposition of water react with the monomer generating monomeric radicals. Also, the monomer itself can evaporate into the cavitation bubbles and decompose (on bubble collapse) to create secondary radicals which will also help create more monomeric and other radicals. These radicals then diffuse into the surfactant stabilized monomer droplets and initiate the polymerization reaction converting the droplet into a polymer latex particle. Ultrasound assisted emulsion polymerization has several advantages over the conventional emulsion polymerization [4].

There has also been a large body of work on synthesizing composite emulsions, i.e., those consisting of a polymer in combination with an inorganic phase using ultrasound assisted emulsion polymerization [11–16]. An extensive review on this topic has been reported by Gedanken [17]. The reasons for encapsulating an inorganic material in a polymeric matrix include improving the abrasion resistance of the parent polymer [18], improving the thermal resistance [19], imparting anticorrosive properties [11], etc. The addition of inorganic particles during emulsion polymerization

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http://dx.doi.org/10.1016/j.cej.2013.01.012