

## Short Communication

# Synthesis and Characterization of Carboxymethyl Cellulose/Polystyrene Core-Shell Nanoparticles by Miniemulsion Polymerization

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### **Abstract**

*The first stage to have access to a reservoir is the drilling operation. The proper development of this operation plays a major role in increasing productivity. It must be pointed out that the drilling fluid (mud) is pivotal in achieving this objective. Among these fluids, water-based fluids are the most common ones, which have been utilized to drill approximately 80% of all wells and are more economical compared with oil- or synthetic-based fluids. In this study, synthesis of core-shell carboxymethyl cellulose nanoparticles with polystyrene by miniemulsion polymerization was performed. The synthesized core-shell and modified carboxymethyl cellulose nanoparticles were characterized by particle size analyzer, fourier transform infrared spectroscopy, thermo gravimetric analysis and scanning electron microscope. The result showed that the average sizes of carboxy methyl cellulose and core-shell nanoparticles are approximately 47 and 80 nm, respectively. The core-shell nanoparticles have spherical shape with a smooth outer surface. Indeed, the produced core-shell improved the thermal resistance of carboxymethyl cellulose nanoparticles in comparison to bulk carboxymethyl cellulose.*

**Keywords:** Miniemulsion, Core-shell, Nanoparticles, Polystyrene, Carboxymethyl cellulose.

### **1. INTRODUCTION**

Nanoparticles which have a core-shell configuration are formed from a dense core and a shell around the core; include a wide variety of different materials such as inorganic/inorganic, inorganic/organic, organic/inorganic and organic/organic. The core-shell contains an inorganic core and a polymer shell, which gives the possibility of combining the advantages of different materials. Thus the core-shell is very useful when material with a multiple desired property is needed.

Core-shell nanoparticles can be prepared through heterophase polymerization [1], heterocoagulation [2], layer-by-layer self-assembly method [3] and chemical

reduction [4]. Among these methods, heterophase polymerization is by far the most frequently used technique. There are several heterophase processes that allow the formation of polymeric nanoparticles in water; the most well-known method is the emulsion polymerization technique, which is used in many industrial applications. In this method, the nanocomposite particles are prepared by carrying out an aqueous phase polymerization in the presence of inorganic particles by conventional emulsion polymerization [5] inverse emulsion polymerization [6], inverse microemulsion polymerization [7],

suspension polymerization [8], miniemulsion polymerization [9] dispersion polymerization [10, 11], and so on.

Ding et al. described the encapsulation of silica nanoparticles with polystyrene via in situ emulsion polymerization [12]. Yang et al. and Biswal et al. reported the synthesis of Carboxymethyl cellulose and polyacrylamide graft copolymer [13, 14]. Pu et al. prepared the composite of SiO<sub>2</sub> nanoparticle with poly (methyl methacrylate) [15]. Mahdavian et al. described the preparation and characterization of nano Al<sub>2</sub>O<sub>3</sub>-poly (styrene-methyl methacrylate) particles via miniemulsion polymerization [16]. Liu studied the preparation of mono dispersed core-shell zinc oxide with polystyrene via microemulsion polymerization [17]. Layeghi et al. studied the Polyaniline-Polystyrene-ZnO Nanocomposite via chemical polymerization [18]. Olad et al. reported the synthesis of polyaniline (PANI) with natural clinoptilolite (Clino) by chemical oxidative polymerization [19]. Rong et al. prepared Titanium dioxide nanoparticles/polystyrene composite via radical polymerization [20]. Mahdavian et al. prepared nano composite of SiO<sub>2</sub> with poly (styrene/methyl methacrylate) via emulsion polymerization [21]. Romio et al. described the encapsulation of magnetic nickel nanoparticles via inverse miniemulsion polymerization [22]. Yong et al. reported the synthesis of core-shell titanium/polystyrene core-shell via miniemulsion polymerization and they investigated the morphology, composition and suspension rheology [23]. Zengeni et al. encapsulated clay by Ad-mini emulsion polymerization [24]. Faridi majidi et al. presented the encapsulation of magnetic nanoparticles with polystyrene via emulsifier-free miniemulsion polymerization [25]. Galindo et al. studied the encapsulation of silver nanoparticles in a polystyrene matrix by miniemulsion polymerization and its antimicrobial activity [26]. Mahdavian et al. studied the

preparation and characterization of core-shell morphology (I, II) Fe<sub>3</sub>O<sub>4</sub> nanoparticles with poly (butyl acrylate-styrene) via miniemulsion polymerization [27, 28]. Mirzataheri et al. synthesized the core-shell morphology of cloisite 30B with poly(styrene-co-butyl acrylate) via miniemulsion polymerization [29]. Xu et al. encapsulated iron oxide nanoparticles by polyacrylamide via inverse miniemulsion polymerization [30]. Sun et al. studied the synthesis and characterization of polystyrene encapsulated laponite composites via miniemulsion polymerization [31]. Reculosa et al. reported the synthesis of raspberrylike silica/polystyrene nanocomposites [32]. Tiarks et al. encapsulated carbon black by miniemulsion polymerization [33]. Csetneki et al. prepared magnetic polystyrene latex by using miniemulsion polymerization [34].

Miniemulsion polymerization process is a very versatile technique for the formation of a broad range of polymers and structured materials in confined geometries [35].

Recently, miniemulsion polymerization has been found to be a particularly attractive way to obtain core-shell nanoparticles and is subject to numerous theoretical [36] and experimental [37] studies.

Among soluble polymers, carboxymethyl cellulose (CMC), nano scale and bulk, are very important chemicals used in industrial oilfield production. Such as filtrate reducer in drilling fluid and viscosifier in fracturing operation. But the intrinsic properties of CMC (nanoscale and bulk) are limited by increasing temperature. Recently, the core-shells of polyacrylamide or polystyrene with carboxymethyl cellulose (CMC) were studied by different methods, but no effort has been seen at the nano scales.

In this study, the core-shell of CMC nanoparticles with polystyrene was synthesized to prepare the spherical

nanosize CMC/polystyrene nanocomposite particles via miniemulsion polymerization. For this purpose, CMC nanoparticles were coated with oleic acid to obtain modified nano CMC. Then they were incorporated into the miniemulsion polymerization in order to obtain the core-shell particles with polystyrene as the shell and modified CMC nanoparticle as the core.

## 2. EXPERIMENTAL

### 2.1. Material

NanoCMC was purchased from Nano Technology Research Institute. Hydroquinon, benzoyl peroxide, sodium dodecyl sulfate (SDS), hexadecane (HD), calcium chloride, hydrochloric acid (36%), ammonia and styrene with 20 ppm inhibitor (analytical grade) were purchased from chemical Merck Co. Span 80 was supplied by Applichem Co.

### 2.2. Remove of Inhibitor from Styrene Monomer

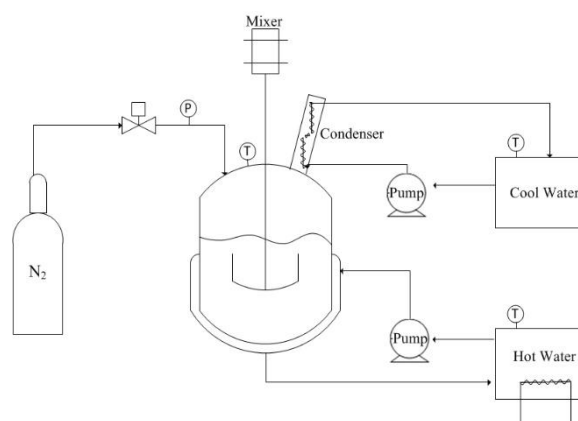
The amount of styrene (0.14 mole) was washed twice with aqueous sodium hydroxide (5-10 wt.%). Styrene was separated from the separatory funnel. Then it was washed by distilled water in a same way. Finally, calcium carbonate (10-12 wt.%) were added into the styrene in order to dry and stored at 0 °C.

### 2.3. Modification of Nano-CMC with Oleic Acid (m-nCMC)

NanoCMC (0.05 gr), oleic acid (0.05 ml) and distilled water (5 ml) were added into the reaction vessel then the solution was sonicated. The ammonia (0.25 ml, 25 wt.%) was added to the mixture, sonicated and stirred with magnetic stirrer. The mixture was demulsified by adding HCl dropwise. The liquid phase was separated by centrifuge. The obtained precipitate was washed twice with methanol, and then it was dried at room temperature.

### 2.4. Synthesis of Core-Shell m-nCMC with Styrene

The process to obtain core-shell was as follows: The mixture of m-nCMC (0.05 gr), Styrene (0.13 mole), HD (12 wt.%) and span80 (3 wt.%) were added in a beaker and mixed by ultrasonic. Also a solution of SDS (2.5 wt.%) and distilled water (60 ml) were mixed in another beaker and sonicated. Then two above mixtures were mixed by ultrasonic irradiation. The formed miniemulsion and benzoyl peroxide (2.5 wt.%) were poured into a round bottomed reactor of 500 ml volume under nitrogen atmosphere and condenser with a mechanical fixed at 300 rpm during the process. The schematic of the core-shell synthesis is illustrated in Figure 1. The process was completed after 8-9 hr. The temperature (70 °C) and mechanical stirring rate were constant in the whole process. The product was cooled at the room temperature. Homopolymers were separated by soxhlet extraction system. Sampling was carried out every 30 min along the polymerization process. Each sample was inhibited by using the solution of hydroquinone (1 wt.%) /methanol. Eventually, samples were dried at room temperature and used to calculate the conversion percent [16].



**Figure 1.** A schematic of core-shell synthesis process.

### 2.5. Characterization

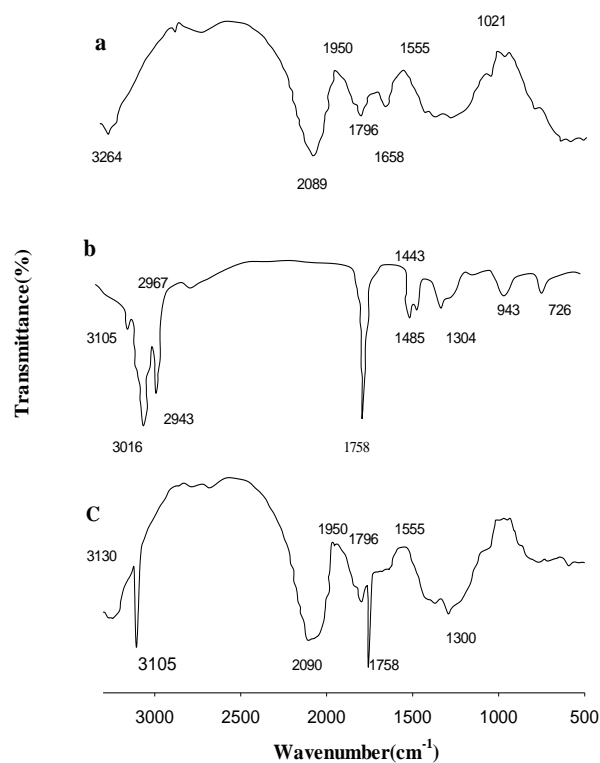
To determine the characteristics of the m-nCMC/polystyrene synthesized core-

shell, fourier transform infrared spectroscopy (FTIR), particle size analyzer (PSA), scanning electron microscope (SEM) and thermo gravimetric analysis (TGA) were used. FTIR analysis is used to verify the modification of nanoCMC surface with oleic acid. The FTIR of nanoCMC, oleic acid and nanoCMC modification in KBr pellets were recorded on a FTIR BRUKER-IFS 48 spectrophotometer (Germany). PSA is used to determine distribution of nanoCMC particle size. PSA of nanoCMC was recorded by using a Horiba-LB-550 PSA. The thermal analysis of nanoCMC, polystyrene and m-nCMC/polystyrene core-shell was carried out with a Perkin Elmer Pyris thermal analyzer. TGA analysis determines the verification of synthesized core-shell and also the thermal resistance of the synthesized core-shell. TGA was performed up to a temperature of 700 °C, starting from room temperature under nitrogen flow (20 ml min<sup>-1</sup>) and a heating rate of 10 °C min<sup>-1</sup> was maintained during the process. SEM is a system that determines the morphology and size of core-shell. The characterization of the core-shell morphology was analyzed by SEM.

### 3. RESULTS AND DISCUSSIONS

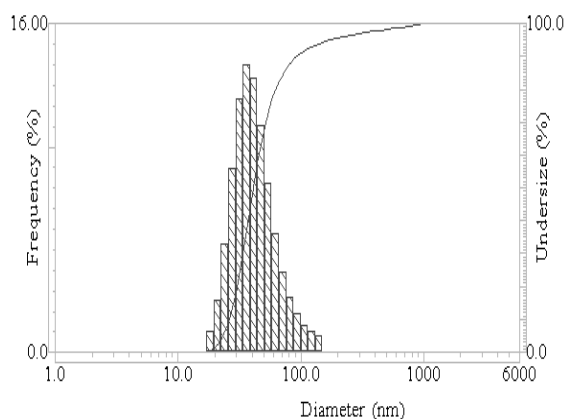
Figure 2 shows the FTIR spectrum of nanoCMC, oleic acid and m-nCMC. The comparison between FTIR spectra of nanoCMC and m-nCMC indicates the existence of oleic acid characteristic peaks in the m-nCMC that is due to the adsorption of oleic acid on the nanoCMC surface. The characteristic peaks are at 1,710 cm<sup>-1</sup> (C=O bond) and the stretching C–H bonds at 3000–3200 cm<sup>-1</sup>. PSA of nanoCMC is depicted in Figure 3, which shows a narrow, symmetrical distribution around 47 nm. The TGA curves of nanoCMC, polystyrene, and core-shell are shown in Figure 4. In the case of nanoCMC, the weight loss is due to the loss of CO<sub>2</sub> from the polysaccharide. The rate of weight loss increases with increasing temperature. Figure 4 shows the

TGA data for polystyrene degradation. Experimental results show that the degradation starts at about 385°C. It also indicates that the breaking begin of the C–C bond for polystyrene degradation occurs at the same temperature. It is obvious from the TGA curves that m-nCMC/polystyrene core-shell is thermally more stable compared to nanoCMC and polystyrene. So, from the TGA results it is concluded that the grafting of polystyrene chains onto the polysaccharide backbone enhances the thermal stability of the polysaccharides. Thus, m-nCMC/polystyrene core-shell has a higher thermal stability in comparison with nanoCMC.

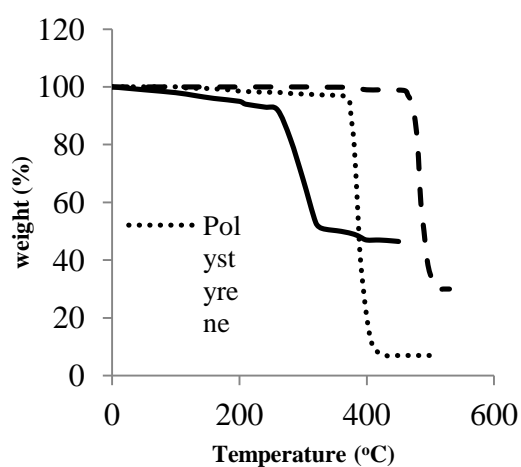


**Figure 2.** FTIR spectrum of (a) nanoCMC, (b) oleic acid and (c) m-nCMC.

The SEM image of the m-nCMC/polystyrene core-shell is represented in Figure 5. The core-shell nanoparticle has a spherical shape with smooth outer surface. The observed core-shell size in the SEM picture is within the range of 80 nm.



**Figure 3.** Particle size analyzer of *m-nCMC/polystyrene core-shell*.



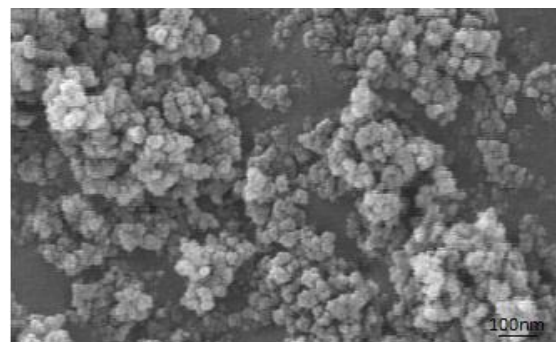
**Figure 4.** TGA curves of *nanoCMC, polystyrene and core-shell*.

#### 4. CONCLUSION

The synthesis and characterization of CMC nanoparticles core-shell with polystyrene via miniemulsion polymerization process have been presented in this work.

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**Figure 5.** SEM image of *m-nCMC/polystyrene core-shell*.

NanoCMC have modified with oleic acid which causes nanoCMC change into hydrophobic nanoparticles and verified by FTIR analyzer. The synthesized core-shell nanoparticles were analyzed by TGA and SEM, in order to prove the morphology and particle size distribution. PSA analysis result shows that the average size of nanoCMC is about 47 nm. The TGA analysis results prove the grafting core-shell synthesis. And also the synthesized core-shell is damaged at a higher temperature rather than nanoCMC and polystyrene. The SEM morphology analysis of *m-nCMC/polystyrene core-shell* showed that the size of produced core-shell is approximately 80 nm and also represented the spherical shape of the core-shell. According to results obtained, it can be predicted that the CMC nanoparticles core-shell with polystyrene can be applied in some processes like EOR application and in pipe flow to decrease the drag force coefficient.

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