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Encapsulation of Carbon Black through Miniemulsion Polymerization as Hydrophobic Coating for Packaging Materials

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ABSTRACT

Polymer encapsulations of three different grades of easy dispersible carbon black, Nipex 35 with particle size 14, Nipex 90 of particle size 25 and Nipex 150 with particle size 31 nm were carried out using silica particles as a surfactant. The encapsulation was carried out by miniemulsion polymerization of styrene/butyl acrylate as a hydrophobe coating in presence of hexadecane. High initiator percentage was essential because carbon black is an efficient radical trap. The morphology of the prepared encapsulated particles was investigated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The effect of hydrophobic coating on the life time of the food emulsion model of soybean soluble polysaccharides was studied. Moreover, the stability of emulsion that prepared by different Nipex grades were studied to find the most appropriate carbon black for emulsion stabilization.

Keywords: Carbon black; Encapsulation; Emulsion polymerization; Packaging Materials

INTRODUCTION

Miniemulsions are dispersions of two immiscible phases, an aqueous phase and an oil phase. The oil droplets are of 30–200 nm size and can be prepared by sonicating or shearing of a system that contains oil (monomer), water, surface active agent (surfactant), and hydrophobe [1-5]. Generally, miniemulsion polymerization differs from traditional emulsion polymerization in the particle nucleation's (formation) mechanism.

Miniemulsion polymerization has been used to encapsulate various types of inorganic materials with definite applications in many fields [6-11]. Carbon nanotubes (CNT) and carbon black (CB) are considered the most encapsulated carbon base inorganic materials. The efficiency of CB depends greatly on its particle size and dispersion or spreading. CBs are widely used to enhance formulations and provide extensive flexibility in meeting specific color requirements and as a reinforcing agent in various industries. Therefore, in this study our goal is to encapsulate CB by polystyrene/polybutylacrylate copolymer through miniemulsion polymerization technique; which is used to produce high efficient coating nanoparticles dispersed in aqueous medium. There are two principal challenges in CB encapsulation: [1] controlling the amount of encapsulated CB; and (2) degree of polymerization through the encapsulation process. In addition, when producing unique encapsulated coating agents in a specific copolymer, the build-up of specific size of polymer coating particle, with aim of producing a high qualified stable hydrophobic thin film that increases polysaccharides emulsion stability, is another challenge of encapsulation of CB through miniemulsion polymerization. Soybean soluble polysaccharides, an ingredient extracted from the byproduct

of the isolation of soybean, were used to prepare a model of an emulsified food product to study its stability in the presence and absence of a hydrophobic coating layer.

The formulations of CBs' stable dispersions in water area long encountered problem of material science, either for pigmentation purposes or as reinforcing filler particles in the polymers preparations [12]. Compared to other nanoparticles that used for embedding, the primary particle size of CB is relatively small and the inter-particle forces are high; therefore, aggregates and agglomerates are easily formed, reducing their application properties. It has been reported that choosing the right concentration of surfactant is essential in miniemulsion polymerization [13]. Consequently, to prepare hybrid nanoparticles by miniemulsion polymerization, a chemical modification using inorganic particles is desirable for physical modification.

According to previous literature which missed valuable applications in coating technology though inorganic encapsulation in packaging field, This work pay an attention to encapsulate cheap, healthy and aqueous dispersion of inorganic material in polymer matrix as hydrophobic coating. Also, it also aims to study the stability of the prepared hydrophobic coating on the life time of food emulsion in order to be used in packaging industry.

MATERIALS AND METHODS

2.1 Materials.

Silica particles (Wacker Chemicals Middle East), Styrene (98 %, Aldrich) and n-butyl acrylate(98 %, Aldrich) were purified two times using sodium hydroxide treatment and distilled over CaH₂ freshly before used. Three types of carbon black (Nipex® 35 of pH = 9.5, Nipex® 90 of pH = 8.3 and Nipex® 150 of pH = 3.5 with particle size 14, 25 and 31 nm respectively) from Evonik, Germany) were used in encapsulation through miniemulsion polymerization technique. hexadecane (HD, >98%, Fluka) were used as received.

2.2 Encapsulated Carbon Back through Miniemulsion Polymerization.

In three neck tube 16 g styrene and 4 g of n-butyl acrylate and 757 mg hydrophob (hexadecane, HD) were mixed and added to a solution of 216.8 mg amphiphilic silica nanoparticles (Ludox) in 71.28 g of water. The mixture was degassed (vac/N₂, followed by stirring 22 min under N₂ at 150 min⁻¹). The mixture was stirred for 1 hour at 800 min⁻¹. After that, miniemulsion was prepared by ultra-sonication for 13 minutes (Amp. 80%) with an ultrasonic disintegrator Qsonica, USA. A slight stream of nitrogen was applied and the emulsion was cooled with ice water. Different types of CB (NIPEX-35, NIPEX-90 and NIPEX-150) were dispersed in 22 ml water containing 40 mg Ludox, then sonified for 5 min at 25% amplitude and added to reaction mixture. The formed miniemulsion was transferred to the reaction vessel. After short degassing, the temperature was raised to 72°C. After reaching T, an aqueous solution of initiator (360 mg KPS in 7.2 g water, degassed under N₂ for 30 minutes) was added. The reaction was carried out at 800 rpm for 6hrs. Then the mixture was cooled to 25°C.

2.3 Preparation of oil in water emulsions from soy polysaccharide.

Soy polysaccharide was dissolved in water. Then, it was stirred for overnight, pH adjustment, and the addition of NaN₃, the polysaccharide stock solution with pH 3.3, polysaccharide apparent concentration 50 mg/mL, and NaN₃ concentration 0.02% was obtained. The polysaccharide concentration was simply calculated according to the powder weight of soluble soybean polysaccharide. Soybean oil was added up to a volume fraction of 10%. The mixture was pre-emulsified at 20,000 rpm for 30 sec, using a homogenizer (IKA T 18 Ultra Turrax, Germany), and was immediately emulsified using a sonification homogenizer (Qsonicasonicator, USA) at 60 % Amplitude for 6 min. After that the emulsion was poured in measuring cylinder coated with prepared hydrophobic copolymer to investigate its stability. For all emulsion samples the measured volume for stability monitoring was 10 ml. The continuous phase was inferred by (drop test) observing whether a drop of emulsion was dispersed or remained when added to the pure oil or pure water emulsion. Water continuous emulsions (oil-in-water, o/w) prefer to disperse in water and remain as drops in oil, while oil continuous emulsions (water-in-oil, w/o) prefer to disperse in oil but remain as drops in water

2.4 Gel Permeation Chromatography (GPC).

Molar masses were measured by GPC Agilent Series 1100, CHCl₃; 1 mL/min, RI detector, columns PL-MIXED-B-LS (300x7.5 mm) and 10mm PS-gel (Agilent Co., USA).

2.5 Thermal Gravimetric Analysis.

Pyris 1 TGA PerkinElmer Instruments, USA is a vertical design with a high sensitivity balance and quick response furnace. Measurements were performed at a heating rate of $\pm 5^\circ\text{C}/\text{minute}$ under nitrogen with temperature range from the room temperature up to 800°C . The instrument was calibrated with Curie-point-standard (nickel and iron alloy).

2.6 Scanning Electron Microscope.

SEM Ultra 55 plus (Zeiss Co., Germany) was used. the thinned dispersions from the DLS measurements were used to prepare the samples on C-pads, air dried and sputtered with 3 nm Pt. Alternatively, the powder of dried precipitated samples was applied on C-pads and sputtered with 3 nm Pt was used.

2.7 Transmission Electron Microscope Measurement.

The inspection of polymer matrix particles (polystyrene) was carried out using transmission electron microscope. The examination was carried out for very dilute suspension of the corresponding polymer latex in distilled water using TEM photographs of Jeol JEM- 1230 Type and an acceleration voltage of 80 Kv. The microscopy probes of the polymer particle samples were prepared by adding a small drop of the distilled water dispersions onto a Lacey carbon film-coated copper grid and was dried in air.

RESULTS AND DISCUSSION

3.1 Comparison of the measured particle size with different investigation techniques.

As presented in table 1 and figure 1, there is a good agreement of particle size measurements between DLS and SEM for most samples. Some samples show small differences in particle size measurements, especially in SEM, which is likely due to dilution of SEM samples before detection. Generally there is a narrow distribution of the prepared polymer sizes is exhibited in this table that ensures the uni-modal distribution of the particles. As it is known that the importance of hydrophobe is to stabilize mini-droplets by decreasing Ostwald ripening [14].

Table 1. Particle size with different investigation techniques (DLS, SEM and TEM)

Sample code	Monomer	CB, a (5%) & b (10%)	Particle size (DLS) nm	Particle size (SEM) nm	Particle size (TEM) nm
PS	St	----	65	30-80	30-50
PBA	BA	----	81	30-70	30-40
PS/PBA	St/BA 75/25	----	87	40-50	30-50
EM1	St/BA 75/25	NIPEX-35 ^a	98	50-80	30-50
EM2	St/BA75/25	NIPEX-90 ^a	93	60-90	40-60
EM3	St/BA75/25	NIPEX-150 ^a	84	70-80	40-50
EM4	St/BA75/25	NIPEX-35 ^b	106	50-90	30-40
EM5	St/BA 75/25	NIPEX-90 ^b	117	30-50	40-60
EM6	St/BA 75/25	NIPEX-150 ^b	108	40-80	40-50

3.2 SEM micrographs of various recipes prepared by miniemulsion polymerization:

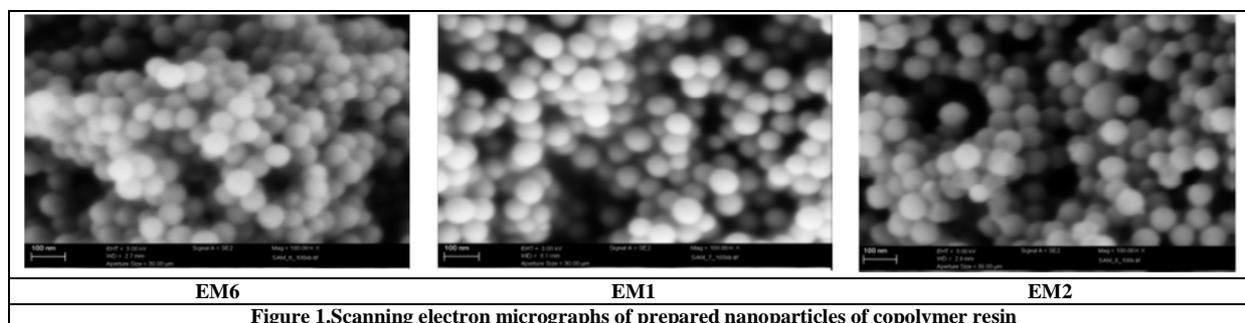


Figure 1. Scanning electron micrographs of prepared nanoparticles of copolymer resin

Scanning electron micrographs of miniemulsion polymerization series in the presence and absence of encapsulated CB are presented in figure 1. Spherical polymer particles were detected with narrow particle size distributions, ranging from 40-90 nm. Moreover, the figure shows that surface of these particles is smooth and the particles have

uni-modal dispersed. DLS and SEM results are in agreement in terms of particle size, with little deviation due to differences of measurement state (in solution in the case of DLS and solid dry state for SEM). Polymer particles can swell and shrink corresponding to the nature of the copolymer in solution during DLS measurement. In the case of SEM, the particle can be extrovert, to give large sizes or highly dried under vacuum conditions to give small sizes.

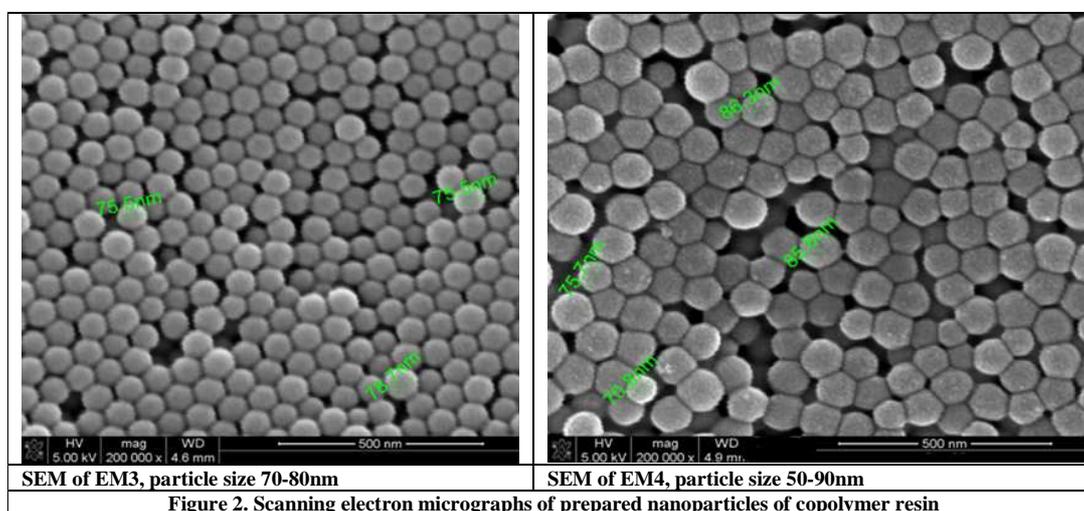


Figure 2. Scanning electron micrographs of prepared nanoparticles of copolymer resin

As it is shown in Figure 2, the production of polymeric nanospheres or nanocapsules of unique characteristics by miniemulsion polymerization increases its commercial interests. As it is clear, the miniemulsion polymerization produced high stable aqueous dispersions of droplets (50- 85 nm). Moreover, a relatively narrow size distribution, smooth and spherical morphology of particles were observed.

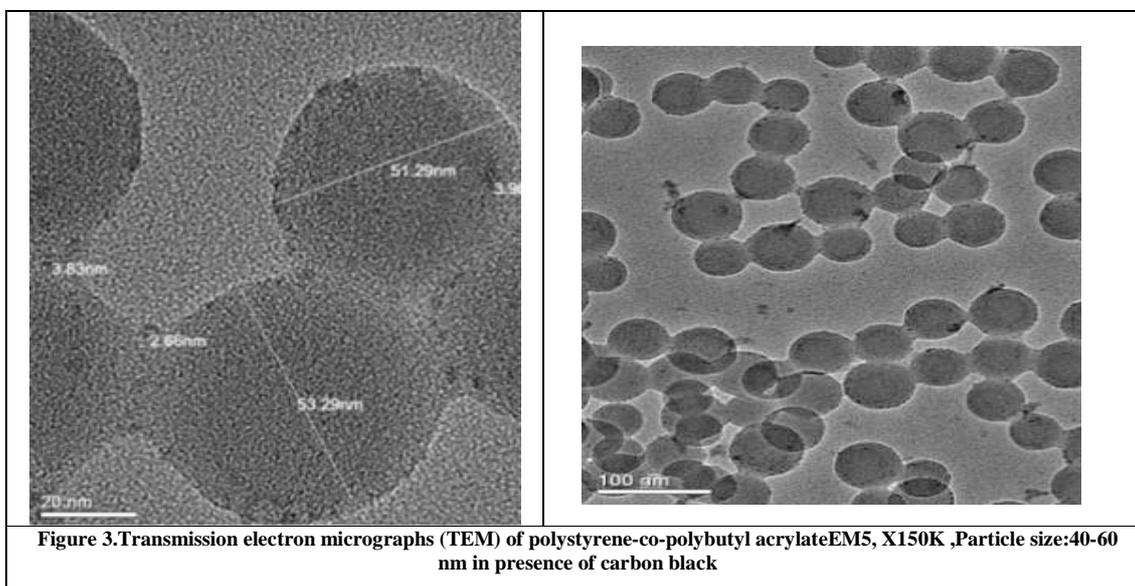


Figure 3. Transmission electron micrographs (TEM) of polystyrene-co-polybutyl acrylate EM5, X150K, Particle size: 40-60 nm in presence of carbon black

3.3 High controlled particle size of hydrophobic coating copolymer:

SEM images of prepared nanoparticles of polymer resin through miniemulsion polymerization techniques are shown in Figure 2. Extra fine particle sizes (20 – 80 nm) with good particle size distributions can be confirmed effective enhancement of sonification process to produce small emulsified droplets. After the polymerization process, droplets of emulsified monomers were controlled polymerized to give most of prepared polymer particles with narrow polydispersity. Ordering of particles in the polymer layer will be enhancing complete coating of packaging can for model emulsified soybean soluble polysaccharides size of hydrophobic coating copolymer.

3.4 TEM micrographs of various recipes prepared by miniemulsion polymerization:

The morphological investigation of the prepared polymer resin by miniemulsion polymerization was expanded to include the transmission electron microscopy. Images group in figure 3 to determine the size, shape and uniformity at the optimal conditions of polystyrene-co-polybutyl acrylate in the presence of carbon black.

3.5 Gel Permeation Chromatography:

Gel permeation chromatography is a powerful technique to investigate encapsulation, insertion/interaction of materials. Most GPC chromatographs of emulsion series within retention time, the characteristic time that required for a particular analyte to pass through the system, ranges, similar to a low polydispersity index (from 1.8 to 5.4) and a range of molecular weights for prepared polymer resin through miniemulsion polymerization techniques.

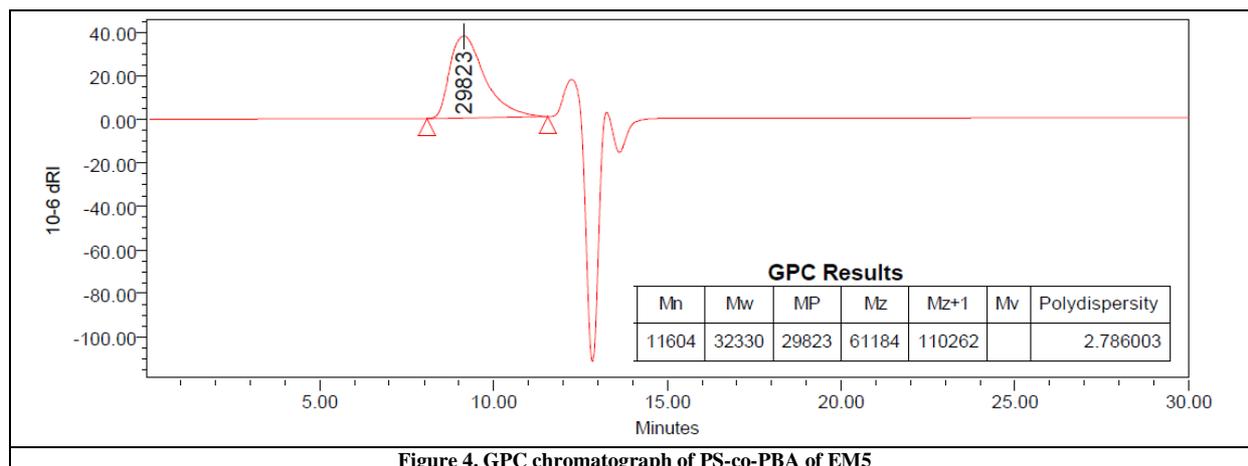


Figure 4. GPC chromatograph of PS-co-PBA of EM5

Diversity in molecular weight was reflected in particle size of encapsulated seed. Also, it can be applied for further study with its effect in coating homogeneity test and coating quality.

The results in figure 4 ensure the dissimilarity of number average (M_n), weight average (M_w) and higher average molecular weights (M_z and M_{z+1}) that a polydisperse polymer is formed ($PDI = 2.78$) i.e. $PDI > 1$. Moreover, as it was expected the order of these molecular weight averages of polydispersed polymer was $M_n < M_w < M_z < M_{z+1}$. Unimodal chromatograph was illustrated in Figure 4. Without any shoulder or humps from distinguish diversity molecular weight. This is can indicated to recession the chance of polymer chain migration from coated packaging materials to packaged item.

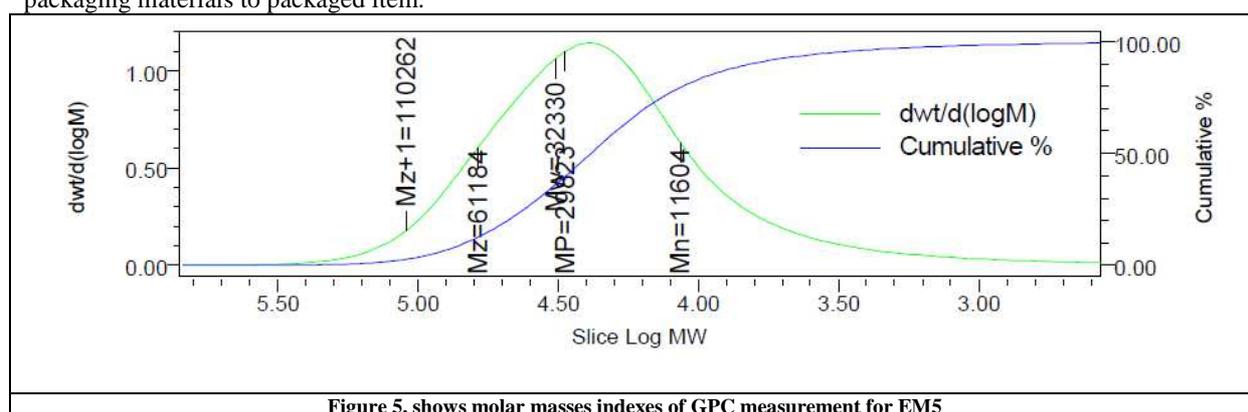


Figure 5. shows molar masses indexes of GPC measurement for EM5

As it is shown in figures 4 and 5 the decreased number average molecular weight is related to the increased initiator percentage, since the average number of monomeric units that incorporated to a polymer chain decreases as there are more growing polymeric chains in the system. Furthermore, the observed large polydispersity index (defined as the weight average to the number average particle radius) is related to the formed mini-emulsion droplets by a shear process which results in a broad droplet size distribution [15].

3.6 Thermal analysis of various copolymers:

Contrary to expectations, the degradation of synthesized copolymers was achieved in a single step. This may be due to the fact that the polystyrene and PBA decomposition temperatures are close to each other's.

Table 2 Thermal behaviors of PS, PBA and PS/PBA copolymers encapsulated CB.

Polymer	^a T _i	^b T _f	^c T _{50%}	Weight loss at 200°C (%)	Weight loss at 400°C (%)	Weight loss at 200°C (%)
PS	344	446	400	2	35	98
PBA	327	458	430	4	23	97
EM1	287	465	421	3	17	96
EM4	278	479	428	2	9	94
EM6	277	458	417	4	18	97

As can be seen from table 2, the decomposition temperatures are in the range of 275-470°C. This means that the synthesized solid-solid copolymers do not degrade or lose weight below 275°C. Consequently, the solid-solid copolymers have a comparable thermal durability because the lower limit of the decomposition temperature (275°C) are much higher than the expected working temperature (shelving temperature) region, or the range of solid–solid phase transition temperature.

3.7 Stability of model polysaccharides food emulsion:

Graduated cylinders coated with encapsulated CB copolymer were used to investigate its influence on the stability of soybean soluble polysaccharides food emulsion model. Hydrophobic coating presence essential improving effect on the stability of polysaccharides emulsion models.

Table 3. Identification of water resolved of EM1, EM2, EM3, EM4, EM5 and EM6 emulsions at different time intervals.

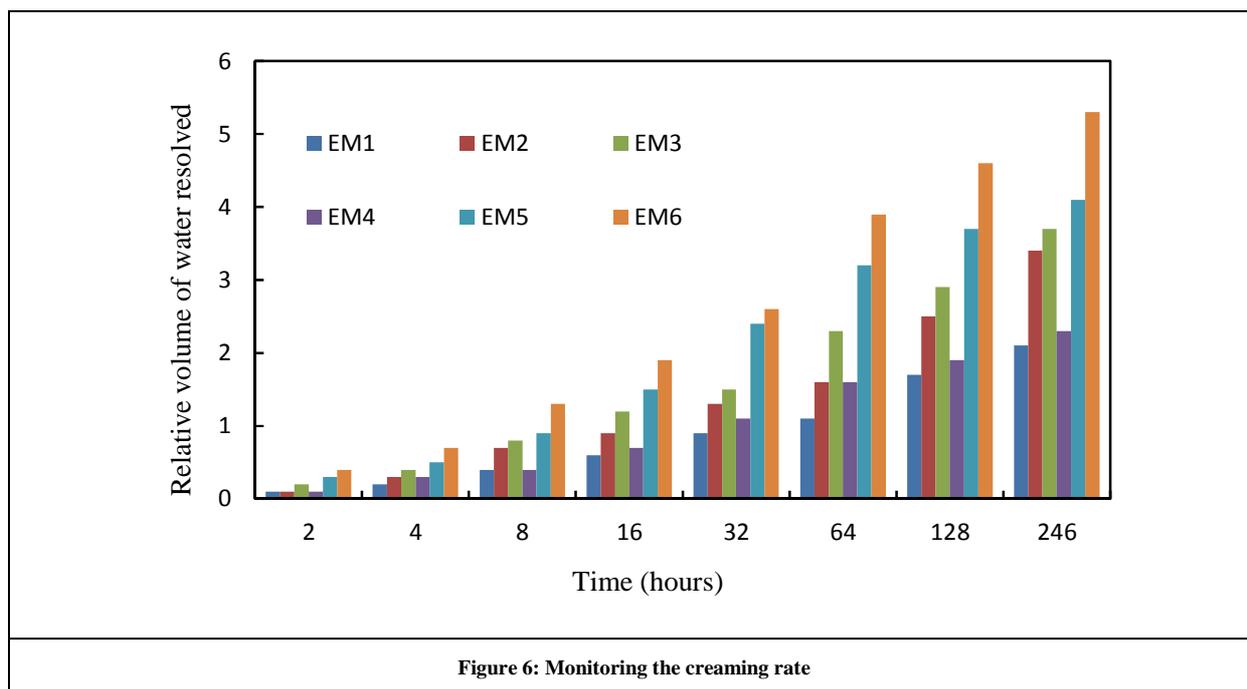
	EM1	EM2	EM3	EM4	EM5	EM6
2 hrs	0.1	0.1	0.2	0.1	0.3	0.4
4 hrs	0.2	0.3	0.4	0.3	0.5	0.7
8 hrs	0.4	0.7	0.8	0.4	0.9	1.3
16 hrs	0.6	0.9	1.2	0.7	1.5	1.9
32 hrs	0.9	1.3	1.5	1.1	2.4	2.6
64 hrs	1.1	1.6	2.3	1.6	3.2	3.9
128 hrs	1.7	2.5	2.9	1.9	3.7	4.6
246 hrs	2.1	3.4	3.7	2.3	4.1	5.3

3.7.1 Determination of emulsion type by drop test.

All emulsion samples were oil in water (o/w) emulsions; where the dispersed phase was oil and the continuous phase was water. Moreover, these emulsion types were proved by drop test.

3.7.2. Stability of O/W emulsions to creaming (water resolved) and coalescence (oil resolved).

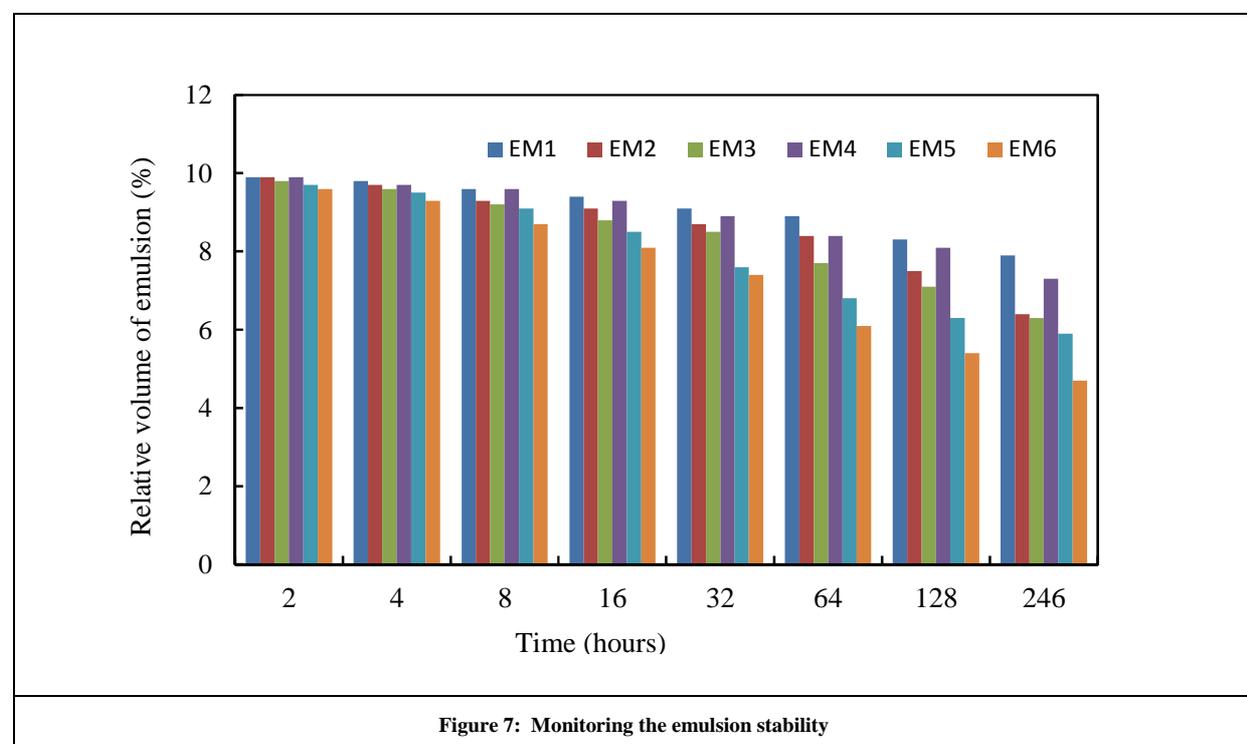
As previously mentioned, all prepared emulsions were o/w. The stability of oil/water(O/W) emulsions to creaming which was evaluated by monitoring the increment of water position with time [16]. In Fig. 6, it is clear that the stability of emulsions to creaming decreases as a consequence of increasing rate of water resolved by time. The highest emulsion stability to water resolved was EM1 emulsions (the smallest rate of resolved water) then those EM4, EM2, EM3, EM5 and EM6 emulsions respectively.



As it is shown in the table 3, there is no oil resolved for all the prepared emulsion which means that the stability for these emulsions to coalescence is very high.

3.7.3. Stability of O/W emulsions.

As shown in Fig. 7, the stability of the prepared emulsions (according to relative volume of emulsions after discarding the resolved water; where there is no oil resolved) decreases with an increase of the time after emulsions



preparations. This stability was in the following order EM1, EM4, EM2, EM3, EM5 and EM6 emulsions respectively. Furthermore, those results are in coincidence with results obtained from Fig.6 and table 3. Finally, it is obvious that the use of Nipex 35 for emulsion stabilization is advisable.

CONCLUSION

Miniemulsion polymerizations were used to prepare various encapsulated CB with copolymer combinations. In addition, many types CB with different particle sizes and pH values were used as inorganic particles in encapsulation reactions with the desired copolymer. The molar ratios were measured for different copolymer samples in the presence and absence of CB. Typical particle sizes of 40–90 nm were prepared by miniemulsion polymerization with narrow polydispersity. Also, the shape and size of the prepared encapsulated particles were investigated by SEM and TEM and exhibited a consistent spherical shape with comparable radii. Hydrophobic coating increases the life time of the food emulsion model of soybean soluble polysaccharides more than uncoated containers. The highest stable emulsion was that prepared by Nipex 35. Therefore, Nipex 35 is the most convenient for emulsion stabilization.

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