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Synthesis and Characterization of PolyHIPEs Composites with Silica and Iron oxide Nanoparticles

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Abstract. This study investigated the synthesis and modification of the properties of polyHIPEs by incorporating co-additives into the polymer matrix i.e. silica (SiO_2) nanoparticles (1 wt%) to improve physical and mechanical properties and iron oxide (Fe_3O_4) nanoparticles (5, 10 and 15 wt%) to induce magnetic and heavy ion adsorption properties. PolyHIPEs composites were prepared in water in oil (w/o) emulsion system using the ratio of organic phase to aqueous phase of 20 to 80 vol%. The physical and mechanical properties of the polyHIPEs composites were found to decrease with SiO_2 and Fe_3O_4 addition while the magnetic and adsorption properties increased with increasing Fe_3O_4 contents. The composites with 1 wt% SiO_2 and 15 wt% Fe_3O_4 exhibited the highest saturated magnetization at 12.9 emu/g and they could be used for adsorption of iron ions (Fe^{3+}) in iron(III) sulfate solution with 98.3 % adsorption at equilibrium.

Introduction

Poly high internal phase emulsions (polyHIPEs) are open porous solid polymer foams usually prepared from polymerization of continuous external organic phase of high internal aqueous phase emulsions (HIPEs). Since the high internal dispersed phase occupies more than 74% of the total volume which corresponds to the maximum packing density of perfect spherical droplets [1], polyHIPEs possess unique properties e.g. low density, high open porosity, high degree of interconnectivity and high surface area. These make polyHIPEs to be considered for various applications that require porous structured materials with high specific surface area such as filtration, ion exchange membrane separation, chromatography, tissue engineering, microelectronic technology and heterogeneous catalytic reaction [1-3]. In order to modify the properties of polyHIPEs, an incorporation of inorganic particles as additives into polymer matrix to form polyHIPEs composites via particle-stabilized Pickering HIPEs processes with and without using surfactants have been investigated extensively [1-10]. Additives such as silver (Ag) nanoparticles [4] were reported to induce antibacterial property, while palladium (Pd) [5] and gold (Au) [6] nanoparticles were found to provide good catalytic activity to polyHIPEs composites. The addition of iron oxide (Fe_3O_4) nanoparticles [3, 7] led to polyHIPEs composite with magnetic property which could be used in heavy metal adsorption applications. Even though, polyHIPEs are potential materials for various commercial applications, poor physical and mechanical properties e.g. chalkiness and brittleness limit their uses in practicality. Therefore, the reinforced additives such as montmorillonite clay [4], carbon black powders [2], titania (TiO_2) [8] and silica (SiO_2) [9-10] nanoparticles have been integrated into polyHIPEs. Haibach et al. reported that reinforced polyHIPEs composites with 1 wt% of SiO_2 nanoparticles could reduce the chalkiness and increase the elastic modulus and crash strength [10]. As the effects of incorporation of SiO_2 together with Fe_3O_4 nanoparticles to generate multifunctional polyHIPEs composites have not been examined yet. This study, therefore, reported the synthesis and effects of integrating of co-additives, SiO_2 and Fe_3O_4 nanoparticles, on the physical, mechanical, magnetic and adsorption properties of the polyHIPEs composites.

Experimental methods

The emulsion HIPEs were prepared by particle-stabilized processes using surfactants in water in oil (w/o) emulsion system using the ratio of organic phase to aqueous phase of 20 to 80 vol%. An organic phase consisted of the required amounts of styrene monomer (C_8H_8, Merck), crosslinking divinylbenzene (DVB, $C_{10}H_{10}$, Merck), sorbitant monoleate (Span 80, Merck) as a non-ionic surfactant, 2,2 azoisobutyronitrile (AIBN, Sigma-Aldrich, 1 mol% of the monomer compositions) as an initiator for polymerization process and the additives, SiO_2 nanoparticles (1 wt %, 10-20 nm, Sigma-Aldrich) and Fe_3O_4 nanoparticles (5, 10 and 15 wt%, < 50 nm, Sigma-Aldrich) were added into a two necked round bottom flask. In order to remove polymerization inhibitor, styrene and DVB were purified by washing with 10 wt%/v sodium hydroxide solution (NaOH, Lab Chemie) and since Fe_3O_4 and SiO_2 nanoparticles are hydrophilic, the additives were surface modified by coating with oleic acid ($C_{18}H_{34}O_2$, Sigma-Aldrich) before incorporating into the polymer matrix [8-9]. The mixture was then stirred with a rate of 500 rpm for 5 min to obtain the homogeneous organic phase. An aqueous phase of 0.34 mol/l (M) calcium cholride dihydrate solution ($CaCl_2.2H_2O$, Riedel-deHaen) used as an electrolyte to suppress the Ostwald ripening [10] was slowly dropped into the continuously stirred organic phase with a rate of 5 ml/min to create emulsions with the high internal aqueous phase in the continuous organic phase. The compositions of the emulsions are summarized in Table 1. After the reaction was completed, the emulsions were polymerized in oven at 80 °C for 24 h. The solid foams were extracted with methanol at 60 ºC for 3 h using Soxhlet apparatus to remove any remaining unreacted chemicals and impurities followed by drying in oven at 80 °C until obtaining constant weight.

Table 1. Compositions of HIPEs

Sample code	Organic phase 20 % [vol%]			Aqueous phase [vol%] 0.34 M $CaCl_2.2H_2O$	SiO_2 [wt%] 10-20 nm	Fe_3O_4 [wt%] < 50 nm
	Styrene	DVB	Span 80			
PolyHIPEs	50	30	20	80	-	-
1%SiO_2	50	30	20	80	1	-
1%SiO_2-5%Fe_3O_4	50	30	20	80	1	5
1%SiO_2-10%Fe_3O_4	50	30	20	80	1	10
1%SiO_2-15%Fe_3O_4	50	30	20	80	1	15

The microstructure of the polyHIPEs composites were examined by scanning electron microscopy (SEM, EVO, Carl Zeiss). The specific surface area, the pore size and pore volume distributions were determined from nitrogen gas (N_2) adsorption/desorption isotherm using Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods (Autosorb-1). The samples were degassed at 95 °C for 12 h before the measurement. The mechanical properties were studied by the universal testing machine in compression mode (LR30K, Lloyd instrument). The cylindrical specimen with 25 mm diameter and 10 mm high was loaded with 5 kN load cell at a rate of 1 mm/min until a displacement limit of 5 mm of the initial specimen thickness was reached. Three specimens were tested for each composition at room temperature. The elastic modulus was evaluated from the initial slope of stress-strain plot while the crush strength was obtained from the stress at the end of linear elastic region. The magnetic properties were investigated using vibrating sample magnetometer (VSM, department of Physics, Kasetsart University, -5 to 5 kOe at room temperature). The adsorption of Fe(III) ions (Fe^{3+}) was studied by soaking 0.25 g of the polyHIPEs composites in an aqueous solution of 3 ppm of iron(III) sulfate nonahydrate ($Fe_2(SO_4)_3.9H_2O$, Lab Chemie) for 24 h at room temperature to obtain adsorption equilibrium. The concentration of Fe^{3+} in the solution was investigated by atomic absorption spectroscopy (AAS, AAS-200, Perkin Elmer). The percentage of adsorption (% adsorption) was determined by the equation: % adsorption = (C_o-C_e/C_o) x 100 % (Eq. 1). When C_o is the initial concentration of Fe^{3+} (3 ppm) and C_e is the concentration of Fe^{3+} after the adsorption (ppm).

Results and discussion

The physical properties of polyHIPEs and polyHIPEs composites are shown in Table 2. The polyHIPEs and polyHIPEs composites showed high specific surface areas (210-668 m^2/g) with total pore volume ranging from 23-65 %. It should be noted that the total pore volumes obtained in this study were less than 74 % which is the lower limit value for polymer foam to be defined as polyHIPEs. However, the microstructure observed from SEM (Fig. 1) showed that the samples possessed open cellular porous structure with highly interconnected open pore network which is the characteristic of polyHIPEs. The polyHIPEs composites with 1%SiO_2-5%Fe_3O_4 exhibited the highest specific surface area (668 m^2/g) and pore volume (65%) corresponding to the small pore size (8 μm) and high degree of interconnected open pore network. These results could be due to the addition of the stabilized particles, oleic acid modified SiO_2 and Fe_3O_4 nanoparticles, leading to the increasing of HIPEs stability by hindering Ostwald repining and droplet coalescence resulting in the polyHIPEs composites with small pore size and high pore volume. These observations are similar to those having been reported for polyHIPEs composites with oleic acid modified TiO_2 and SiO_2 [8-9]. By increasing the Fe_3O_4 contents to 10 and 15 wt%, the polyHIPEs composites consisted of thick wall and non-uniform pore size distribution. Some fused polymer particles were observed in SEM images (Fig. 1(d) and (e)). The unstable structure with low specific surface area of the polyHIPEs composites with 1%SiO_2-10%Fe_3O_4 and 1%SiO_2-15%Fe_3O_4 could be due to an aggregation of excess Fe_3O_4 nanoparticles at w/o interface lowering the HIPEs stability leading to the rupture of droplets during polymerization process [9].

Table 2. Physical properties of polyHIPEs and polyHIPEs composites

Samples	Surface area[a] [m^2/g]	Pore volume[a] [%]	Pore size[a] [°A]	Pore size[b] ±SD [μm]	Pore throat size[b] ±SD [μm]	Physical appearance
PolyHIPEs	420	46	30	11.2 ±2.4	3.3 ±0.6	Chalky
1%SiO_2	455	40	27	10.9 ±4.2	3.2 ±1.4	Less chalky
1%SiO_2-5%Fe_3O_4	668	65	24	8.0 ±1.9	2.9 ±0.9	Less chalky but brittle
1%SiO_2-10%Fe_3O_4	362	46	24	13.1 ±2.0	3.4 ±0.8	Less chalky but brittle
1%SiO_2-15%Fe_3O_4	210	23	19	14.6 ±2.3	2.7 ±1.1	Less chalky but brittle

[a] Estimating from N_2 adsorption/desorption and [b] estimating from SEM images using ImageJ program [11].

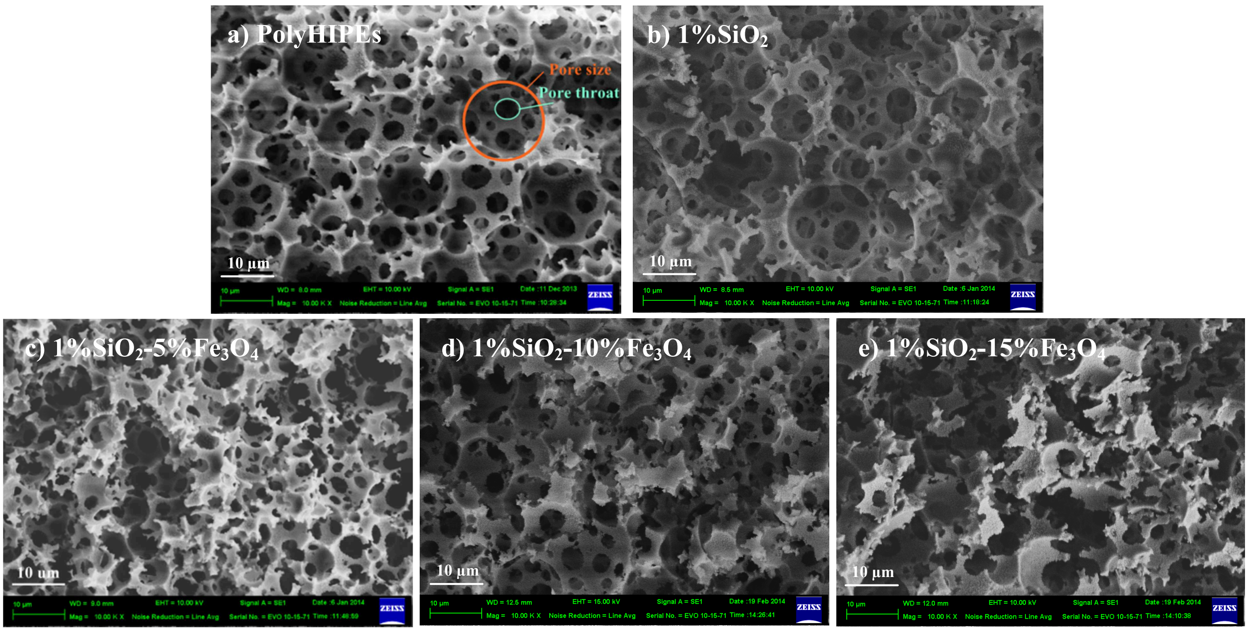

Figure 1. SEM images of a) polyHIPEs, b) 1%SiO_2, c) 1%SiO_2-5%Fe_3O_4, d) 1%SiO_2-10%Fe_3O_4 and e) 1%SiO_2-15%Fe_3O_4.

The mechanical properties of polyHIPEs and polyHIPEs composites are shown in Table 3. The polyHIPEs composites with 1%SiO_2 were less chalky and exhibited the highest elastic modulus (5.82 ±0.04 MPa) and crush strength (0.50 ±0.07 MPa) indicating that SiO_2 nanoparticles could act as reinforced particles [9-10]. By adding co-additives, SiO_2 and Fe_3O_4 nanoparticles, the mechanical strengths including elastic modulus and crush strength of polyHIPEs composites were slightly decreased compared to polyHIPEs and polyHIPEs composites with 1%SiO_2. These results were consistent with the physical appearance that the polyHIPEs composites with SiO_2 and Fe_3O_4 tended to be brittle. For polyHIPEs composites with 1%SiO_2-5%Fe_3O_4, the low mechanical properties could be a result of the high interconnected open pore structure with high total pore volume. While in the case of polyHIPEs composites with 1%SiO_2-10%Fe_3O_4 and 1%SiO_2-15%Fe_3O_4, the non-uniform pore size distribution structure with some fused polymer particles could be responsible for the poor mechanical strength.

Table 3. Mechanical, magnetic and adsorption properties of polyHIPEs and polyHIPEs composites

Samples	Elastic modulus ±SD [MPa]	Crush strength ±SD [MPa]	Saturated magnetization [emu/g]	Adsorption [%]
PolyHIPEs	4.25 ±0.06	0.34 ±0.03	-	-
1%SiO_2	5.82 ±0.04	0.50 ±0.07	-	-
1%SiO_2-5%Fe_3O_4	3.50 ±0.36	0.25 ±0.03	3.6	57.9
1%SiO_2-10%Fe_3O_4	4.50 ±0.30	0.29 ±0.02	9.9	63.6
1%SiO_2-15%Fe_3O_4	2.27 ±0.18	0.16 ±0.03	12.9	98.3
Fe_3O_4 nanoparticles	-	-	68.6	-

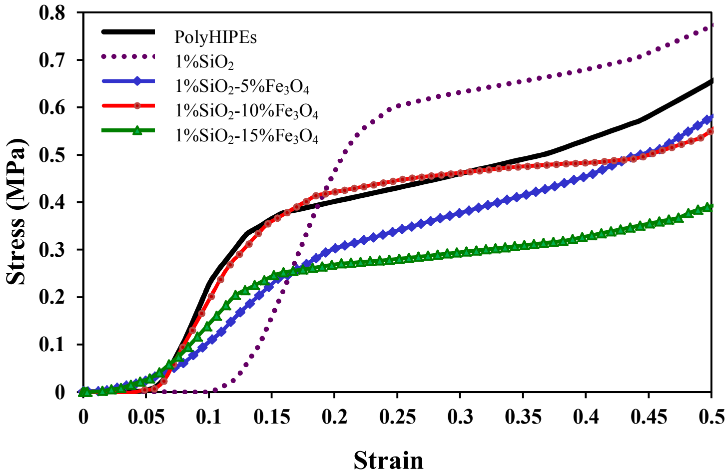

Figure 2. Stress-strain curves of polyHIPEs and polyHIPEs composites.

The magnetizations of the samples as a function of the applied magnetic field (M-H curves) are shown in Fig. 3(a). Fe_3O_4 nanoparticles and the polyHIPEs composites showed pseudo-single domain behavior indicated by narrowed hysteresis loops with coercivity and remnant magnetizations [7]. The saturated magnetization of Fe_3O_4 nanoparticles was 68.9 emu/g (Table 3) which is close to those have been reported in the literature for Fe_3O_4 nanoparticles (56-74 emu/g) [7]. As the magnetic property depends strongly on the sizes of the nanoparticles, the pseudo-single domain behavior of Fe_3O_4 nanoparticles observed in this study could be because the sizes of Fe_3O_4 used (< 50 nm) are larger than the critical size of Fe_3O_4 to exhibit superparamagnetism [7]. The saturated magnetizations (M_s) of the polyHIPEs composites were found to increase with increasing Fe_3O_4 contents indicating the higher degree of Fe_3O_4 integrated into the polymer matrix. The polyHIPEs composites with 1%SiO_2-15%Fe_3O_4 exhibited the highest saturated magnetization at 12.9 emu/g. Magnetic attraction (Fig. 3(b)) confirmed the magnetic property of the polyHIPEs composites induced by the incorporation of Fe_3O_4. Adsorption tests of the polyHIPEs composites in an aqueous solution of 3 ppm of iron(III) sulfate at room temperature for 24 h showed that the polyHIPEs composites could be used for adsorption of Fe^{3+}(Table 3). The %adsorption was dependent on the magnetization in which polyHIPEs composites with the highest magnetization (1%SiO_2-15%Fe_3O_4) exhibited the highest Fe^{3+} adsorption of 98.3 % at equilibrium.

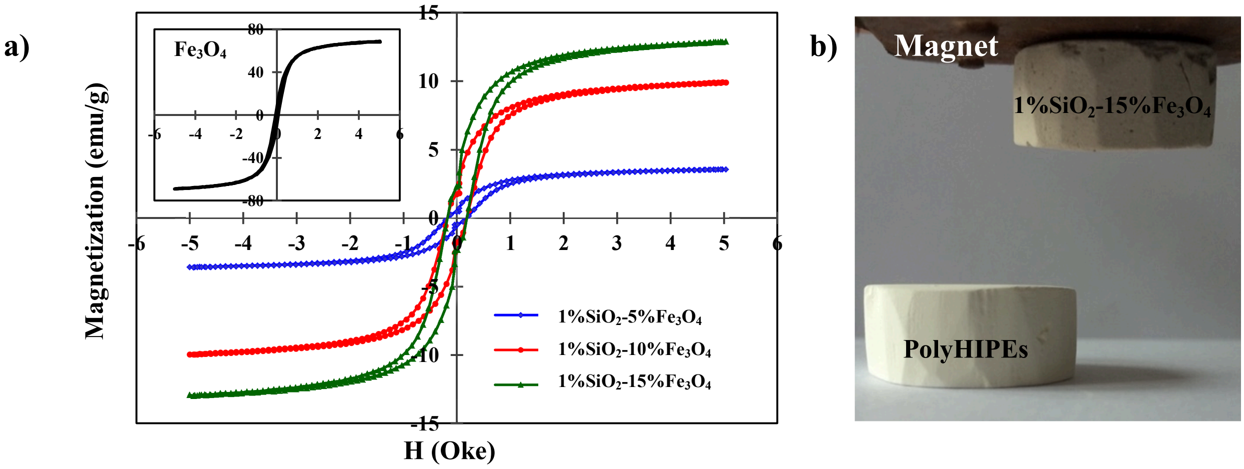

Figure 3. a) Magnetization curves of polyHIPEs composites and Fe_3O_4 nanoparticles (inset) and b) photograph of polyHIPEs and polyHIPEs composites (1%SiO_2-15%Fe_3O_4) with magnet.

Summary

The polyHIPEs composites with SiO_2 and Fe_3O_4 nanoparticles were prepared using particle-stabilized HIPEs with surfactant processes. The physical and mechanical properties of the polyHIPEs composites slightly decreased with incorporating of SiO_2 and Fe_3O_4 while the magnetic and adsorption properties increased with increasing the Fe_3O_4 contents from 5 to 15 wt%. The composites with 1%SiO_2-15%Fe_3O_4 exhibited the highest saturated magnetization of 12.9 emu/g and 98.3 % of Fe^{3+} adsorption at equilibrium. These results suggest that the polyHIPEs composites with SiO_2 and Fe_3O_4 nanoparticles have potential to be developed for heavy ion adsorption applications.

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