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SYNTHESIS OF ACRYLATED PALM OIL NANOPARTICLES USING MICROEMULSION POLYMERIZATION INITIATED BY GAMMA RAY

SINTESIS PARTIKEL NANO MINYAK SAWIT TERAKRILAT MENGGUNAKAN PEMPOLIMERAN MIKROEMULSI YANG DICETUS SINARAN GAMMA

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ABSTRACT

The use of microemulsion in the development of nanoparticle based on acrylated palm oil product is demonstrated. The microemulsion polymerization was initiated by gamma ray (γ-ray) for synthesizing crosslinked nanoparticle. Polymerization of acrylated palm oil in three-component ionic microemulsions was prepared with sodium dodecyl sulphate (SDS) and water. The resulted nanoparticle, before and after initiated by γ-ray, were evaluated in terms of particle diameter, surface charge and molecular structure. Type and concentration of surfactants, monomer concentration, radiation dose and time of storage strongly affected the size, charge and size stability of the particles. For the development of new microscopic polymer acrylated palm oil can be synthesized into nano sized particle and it has potential to be developed in medical devices and controlled-drug-release-applications.

ABSTRAK

Kajian ke atas pembangunan produk nanopartikel menggunakan sistem mikroemulsi berasaskan minyak sawit terakrilat telah dijalankan. Pempolimeran mikroemulsi dicetus menggunakan sinaran gamma untuk mesintesis partikel nano yang bertaut-silang. Pempolimeran minyak sawit terakrilat dalam mikroemulsi ionik tiga komponen adalah disediakan menggunakan Sodium dodesil sulfat (SDS) dan air. Hasil kajian iaitu partikel nano, sebelum dan selepas diuja sinaran gamma, dinilai dari segi diameter partikel, cas permukaan dan struktur molekul. Jenis dan kepekatan surfaktan, kepekatan monomer, dos sinaran dan tempoh storan mempunyai pengaruh yang kuat terhadap saiz, cas dan kestabilan saiz patikel. Pembangunan produk partikel nano adalah boleh disintesis daripada minyak sawit terakrilat dan ia berpontesi dibangunkan sebagai alat perubatan dan berpontensi diaplikasikan sebagai agen pelepasan ubat terkawal.

Keywords: Palm oil, nanoparticle, drug carrier, gamma ray, microemulsion polymerization

INTRODUCTION

Microemulsion system is defined as isotropic, transparent, low viscosity and thermodynamically stable dispersions. This system consist at least three basic components of water, oil and surfactant where their dispersed phase consists of small droplets with diameter in the range of 100-1000A°. Microemulsions were first introduced by Hoar and Schuman in 1943. After almost 40 years, in 1980, Stoffer and Bone developed polymerization in microemulsion system.

Furthermore, polymerization initiated by ionizing radiation can be performed in the bulk, in solution, in emulsion and etc (Ulanski and Rosiak, 2004). According to Wang *et al.* (2007), gamma ray induced dispersed-phase polymerization is a useful technique for preparing novel materials because its advantages such as relatively simple system composing where microemulsion system is prepared without additional initiators, temperature independence and strong penetrability. They also reported that the dispersed phase is water, which is plentiful, nontoxic, environmentally friendly and inexpensive. In addition, Chen and Zhang (2007) mentioned that γ-ray induced polymerization is homogeneously penetrating through the sample. Besides that, from fundamental point of view, radiation-induced initiation showed more advantages compared with chemical initiation. For examples, radiation-induced initiation is essentially temperature independent and at low temperature, polymerizations can be conducted easily. It means that polymerizations of radiation-induced initiation can be conducted at any temperature and at any initiation rate compared with polymerization process of chemical initiation that in the redox systems (Stannett and Stahel, 1991). In addition, Rosiak *et al.* (2003) also reported that a radiation technique is suited for producing nanogels and microgels especially for biomedical applications because they are free of monomers, initiators and any other additives during the process reaction.

Recently, microemulsions have attracted increasing attention as potential drug delivery systems, either as carrier or as bioavailability enhancers for poorly water soluble active pharmaceutical ingredients. Vegetable oils from natural source such

as palm (Amnon and Haim, 2010; Mitra N, 1994), soybean (Corswant *et al.*, 1997, 1998; Mitra *et al.*, 1994), corn (Gupta and Moulik, 2008; Gupta *et al.*, 2006), coconut (Gupta *et al.*, 2006), castor, peppermint (Gupta and Moulik, 2008; Gupta *et al.*, 2006), rapeseed, sunflower, peanut and essential (Wolf *et al.*, 1987) oils are widely used in microemulsions formation. Von Corswant *et al.* (1997) reported that vegetable oils type microemulsions are acceptable for pharmaceutical uses (Corswant *et al.*, 1997). Meanwhile, as reported by Gupta and Moulik (2008), plant and vegetable oils (corn oil, cottonsseed oil, orange oil, clove oil, peppermint oil, eucalyptol oil, and coconut oil), triglycerides and esters of fatty acids (isopropyl myristate (IPM), ethyloleate, etc.) have been used as oil components for preparation of biocompatible microemulsions. They mentioned that microemulsion-based plant and vegetable oils formulations have been found promising in a number of drug delivery applications.

In this present study, combination methods of microemulsion polymerization and radiation crosslinking intiated by γ–ray will be used to prepare acrylated palm oil nanoparticles. The effecting factors of surfactant and polymer concentration, radiation dose and the storage time on the size of nanoparticles were studied.

METHODOLOGY

Materials

The acrylated palm oil (APO) used in this study was synthesized in the laboratory of Radiation Processing Technology Division (BTS), Malaysian Nuclear Agency. Sodium dodecyl sulfate (SDS) (Aldrich Chemical Company) as surfactant. Distilled and deionized water were used through out of this study.

Preparation of nanoparticle

The oil in water dispersed droplets was prepared from oil (APO), water and SDS. Different concentrations of APO, i.e. approximately at 2% (noted as *a*) and 0.2% (noted as *b*), with different concentration of the SDS (above and below SDS cmc region) in an aqueous solution were formulated. The samples which are in the form of microemulsions will be prepared in two different ways; one is for non-irradiated samples and second was irradiated at different doses using a gamma radiation at 1, 5, 10, 15 and 25 kGy. After irradiation, the irradiated micelles were subjected to sizes determination.

Characterization

The samples were filtered for removing of suspended materials or impurity. The sizes of the oil droplets were determined using a dynamic light scattering (Sympatec Nanophox) at a wavelength of 632 nm. Meanwhile, the storage time was arranged from day 1, 7, 14, 30, to day 60. The size of the oil droplets was determined according to the selected period. The same samples were used for the determination of particle surface charge using a zeta potential analyzer (ZetaPlus, BrookHaven). The conductance of the samples was also recorded. The SDS cmc was determined using this conductance data. Infra-red spectrum was performed using Fourier Transform Infrared spectroscopy (Perkin Elmer, Japan). The samples are analyzed using Attenuated Total Reflectance (ATR) method. The Spectrophotometer is setting at spectra in the range of 4000 cm^{-1} to 500 cm^{-1}. Transmission electron microscopy (TEM) was performed using a Zeiss microscope (Jeol, Japan), 120 keV, with magnification of 30000X for the measurement of particle sizes of the micelles in dried form.

RESULTS AND DISCUSSIONS

Critical Micelle Concentration (CMC) and Microemulsion

The CMC of SDS was found approximately at 0.008 Mol, *see* Fig.1. Their micellar sizes are less than 6 nm (Fig.2). The micellar size becomes smaller when SDS concentration was increased (Fig.2). A SDS is well known as ionic group surfactant where it consist negatively charge head. As shown in Fig 3, the SDS micellar at all regions in aqueous solution showed negative surface charges. Furthermore, when APO is fabricated into the micellar the CMC of the SDS was unchanged (Fig.4). The purpose of the micellar is to become as outer shell layer of APO nanoparticle. It help controls the APO nanoparticle stability, *see* Table 1.

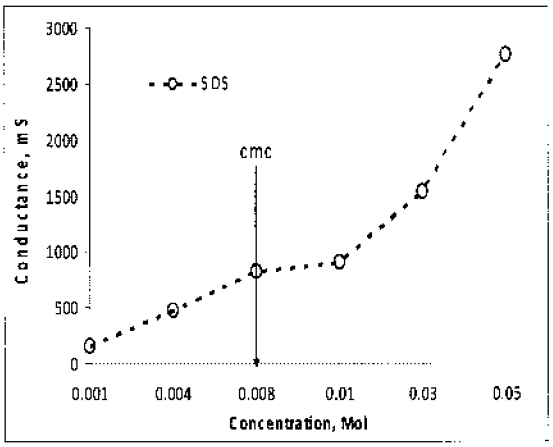

Figure 1: Determination of CMC

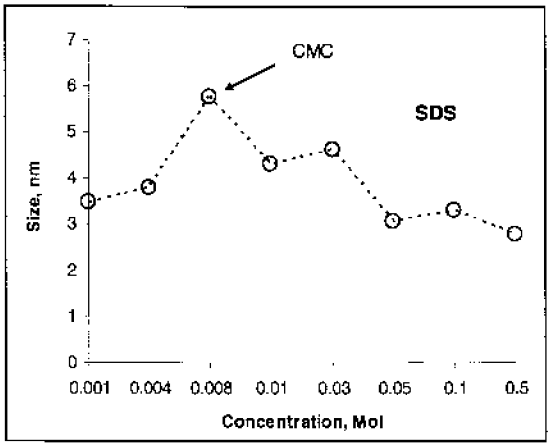

Figure 2: Micellar sizes

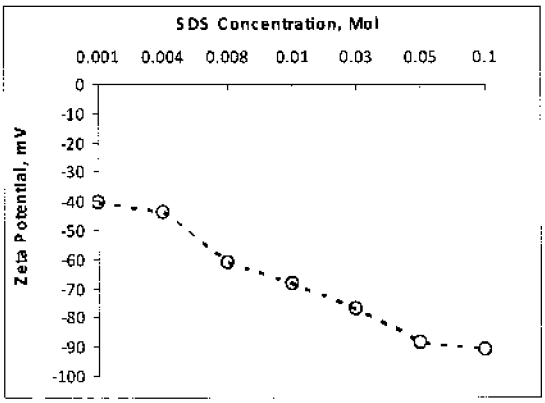

Figure 3: Micellar surface charges

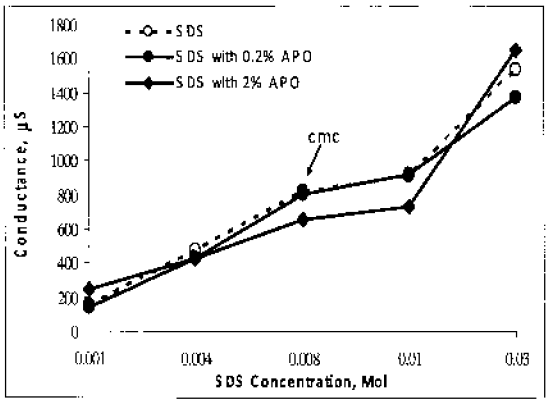

Figure 4: CMC of (Water/SDS/APO) microemulsions

Transmission electron microscopy

Figure 5 showed image of microemulsion systems. The system was semi transparent, isotropic, and homogeneous as shown in Fig.4. Their appearance can be determined at the solution that has less amount of polymer content. The TEM images of nanoparticles were shown in Fig.6. The shape of the (Water/SDS/APO) nanoparticles was spherical and particle size is less than 130 nm (Fig.6).

Figure 5: Microemulsion systems (Water/SDS/APO)

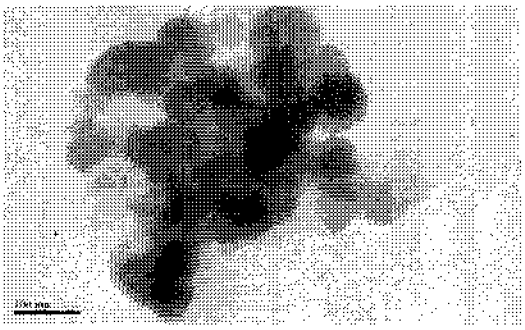

Figure 6: TEM images of nanoparticle

Particle size and size stability

Table 1: Particle size and size stability of oil in water droplets from (Water/SDS/APO) microemulsion

APO concentration	SDS concentration	Particle size stability, nm						Zeta Potential, mV
		Day 1	Day 7	Day 14	Day 21	Day 30	Day 60	Fresh sample
High monomer concentration	SDS free	95.85	155.71	95.75	468.22	585.91	13.63	-61.74
	Below cmc	114.65	112.29	95.79	114.12	106.83	106.48	-90.93
	Near cmc	246.19	242.77	191.61	182.93	282.01	182.70	-125.82
	Above cmc	416.10	342.96	347.43	329.40	444.00	141.38	-124.08
Less monomer concentration	SDS free	95.77	134.44	382.80	134.42	545	132.37	-35.95
	Below cmc	130.12	124.08	144.43	140.93	134.75	127.18	-77.86
	Near cmc	517.12	443.34	398.19	351.2633	98.74	408.93	-144.33
	Above cmc	585.03	554.5	452.25	426.14	95.80	847.65	-118.27

Table 1 showed varieties size of micro/nanoparticles. Size of the particle is influenced by the formulation. Parameters such as monomer (APO) concentration, surfactant (SDS) concentration and the storage time plays important role in this study. In high concentration APO systems, size of the particle increases when the surfactant concentration is above the surfactant's critical micelles concentration (cmc). An ionic based microemulsions with higher APO content shows that the size of the particle is almost unchanged with the storage time until 3 weeks. Then, the particle sizes slightly increases after a month and decrease at two months due to instability. Meanwhile, an ionic based microemulsion with less APO content shows that the size of the particle is slightly decrease in 3 weeks. After a month of the storage time, the particles showed instability. In both mediums, high and less content APO, the microemulsions in SDS free systems showed instability of particle size.

Effect of polymer and SDS concentrations

As discussed above, the results in Table 1 showed that polymer and SDS concentration affects the end products size. Systems with higher APO content resulted in smaller sizes particle and vice versa the result for the formulation with less APO content. When more APO is added, the droplet size decreases is due to the solubility between the APO in solvent. The smaller the droplets are, the larger surface of the particles is. A larger surface requires a larger amount of surfactant to be covered to maintain colloidal stability (Wang *et al*,. 2007). Results showed that APO has good solubility in ionic/SDS surfactant. Add more APO affected increased saturated polymer/surfactant aggregation and thus presence intramolecular interaction between particles. Other factors which influence the product sizes are concentration of surfactants used. If less APO added in systems with high SDS content, systems may resulted more free-APO micelle are formed. Furthermore, particle sizes are grown above the surfactants cmc, in both mediums. Meanwhile, below SDS cmc or at low SDS content systems the stability of the particle is good where sizes of particles are unchanged until 2 months. Surfactant molecules also help to protect the APO from intermolecular reaction and maintain their sizes in aqueous solution. For surfactant free particle, the particle could only maintain their size for less than a week. The size decreasing is due to the flocculation of the particles in system. It showed us that surfactant molecules play major role to control the stability of the particles.

Effect of SDS on the particle surface charge

The zeta potential value was fully depends on the type of the surfactant, as shown in Table 1. The results of zeta potential measurements are related with penetration phenomenon of the surfactant head or their hydrophobic part in microemulsion. Ionic surfactant of SDS gives a negatively charged particle surface, *see* Fig.3. A SDS often gives negative effects on properties of the final polymer latexes (Wang *et al.*, 2007). Furthermore, the degree of the zeta potential is depended on the concentration of the surfactant, as reported in Table 1. Increasing the surfactant volume in microemulsion decreases the zeta potential. Moreover, the zeta potential degree is affected by the volume of monomer presence in the microemulsions. We can assume that at higher water content, lower monomer and higher surfactant concentration in the system, the surfactant molecule is dominantly solubilized, contributing lower zeta potential degree. As shown on the basic analysis of the SDS charges in Fig.3, this study agreed that the systems content a high concentration of SDS.

Effect of irradiation dose on the particle size

Table 2: Dose effect on the particle diameter

APO concentration	SDS concentration	Absorbed Dose, kGy					
		0	1	5	10	15	25
High monomer concentration	Near SDS cmc	246.19	118.33	108.39	114.47	113.72	77.30
	Above SDS cmc	416.10	113.86	104.56	99.04	101.70	103.98
Less monomer concentration	Near SDS cmc	517.12	475.38	95.75	102.97	95.77	95.77
	Above SDS cmc	585.03	330.81	315.34	223.58	235.17	246.25

The microemulsion system with concentration of their surfactants near and above cmc was selected for irradiation. Correlation between the dose effect and the particle sizes is shown in Table 2. After the micellar system was irradiated, the sizes of the particles decrease when the dose of irradiation increased to 1 kGy or higher. A small dose of ionizing radiation is enough to influence the product sizes. The change of the particle size after the micro/nanoemulsion samples triggered to several irradiation doses proved that chains present in the system undergo crosslinking reaction. In these circumstances, reactive species are formed along the polymer chains. At 1 kGy or higher, the crosslinking reaction leads to the formation of fine particles which means that polymer radicals present in the system fabricated into the network. According to Ulanski *et al.* (1998) and Ulanski and Rosiak (1999 and 2004), nanogel formed through intramolecular crosslinking should have different in dimensions and other physiochemical properties. Ulanski and Rosiak (1999) reported that nanogel dimensions should be smaller compared to the parent (origin) polymer because of the shrinkage of the initial loose and mobile polymer coils into more tightly where it internally bound entities. As reported in Table 2, after irradiated the particle size are smaller than the origin size (non-irradiated particle). The study proved that these systems are undergoing the intramolecular crosslinking process.

FTIR analysis

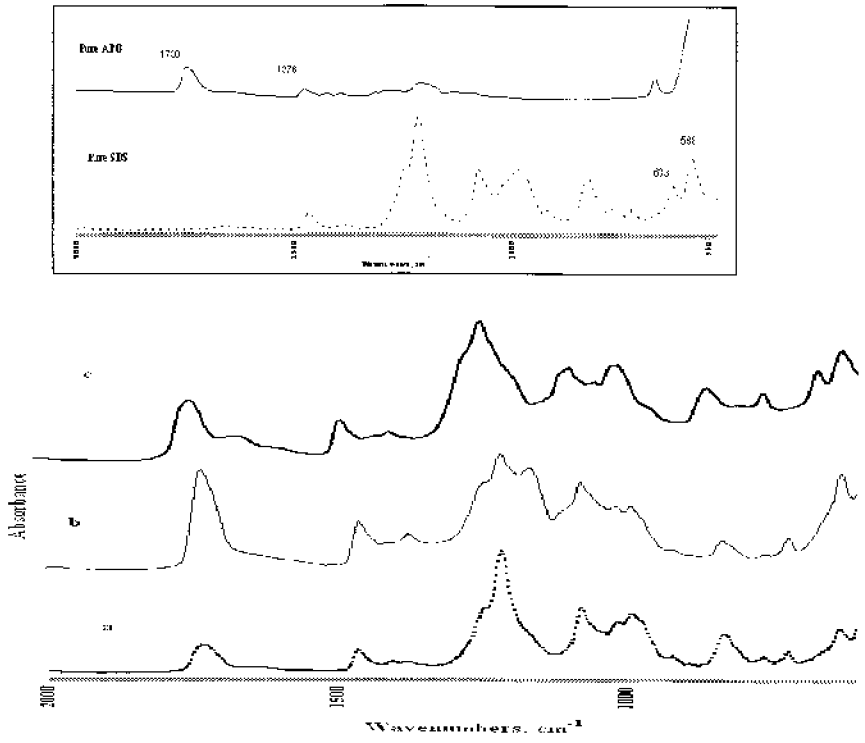

Figure 7: FTIR spectra of (Water/SDS/APO) micro/nanoparticle. (a) non-irradiate; (b) irradiate at 1kGy; (c) irradiate at 25kGy

An IR spectrum of dried micro/nanoparticle which is formulated from micro/nanoemulsion content SS concentration near cmc was studied. Figure 7 shows the spectra of micro/nanoparticle containing high monomer content that has been irradiated at

1 kGy and 25 kGy, the spectra of the non irradiated sample and the spectra of pure SDS and APO. Presence of the SDS in nanoparticle leads to polymer molecular structure changes. The bands at 588cm^{-1} and 633 cm^{-1} are due to the presence of SDS. Meanwhile, the dose effect is leads to attraction of acrylated palm oil chain. The band at 1730cm^{-1} is carbonyl group and 1376 cm^{-1} is carbon-carbon double bond band of APO. However, the SDS is still remained in the nanoparticle even the particle is irradiating at high dose. This radiation technique seemed not eliminated the surfactant. This showed us one of disadvantages using surfactant.

CONCLUSIONS

In this study, acrylated palm oil nanoparticles were prepared with γ-ray radiation induced polymerization in microemulsion systems consist of acrylated palm oil, sodium dodecyl sulphate and water. The particle size decreases with the increase of absorbed dose. In high content of APO/polymer, the systems produced smaller particle size. Meanwhile, the charge and stability of the particles are influenced by the concentration of surfactants, type of surfactant, polymer concentration and time of storage. A surfactant play major role controls the particle stability.

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