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Radiation-Induced Formation of Acrylated Palm Oil Nanoparticle Using Pluronic F-127 Microemulsion System

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ABSTRACT

This study demonstrated the utilization of radiation-induced initiator methods for the formation of nanoparticles of Acrylated Palm Oil (APO) using aqueous Pluronic F-127 (PF-127) microemulsion system. This microemulsion system was subjected to gamma irradiation to form the crosslinked APO nanoparticles. Dynamic light scattering (DLS), Fourier Transform Infrared (FTIR) spectroscopy and Transmission Electron Microscopy (TEM) were used to characterize the size and the chemical structure of the nanoparticles. As a result, the size of the APO nanoparticle was decreased when the irradiation dose increased. The decrease in size might be due to the effects of intermolecular crosslinking and intramolecular crosslinking reactions of the APO nanoparticles during irradiation process. The size of the nanoparticle is in the range of 98 to 200 nanometer (nm) after irradiation using gamma irradiator. This radiation-induced method provides a free initiator induced and easy to control process as compared to the classical or chemical initiator process. The study has shown that radiation-induced initiator methods, namely, polymerization and crosslinking in the microemulsion, were promising for the synthesis of nanoparticles.

Keywords: Acrylated palm oil, nanoparticle, radiation crosslinking, ionizing radiation

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INTRODUCTION

A high energy radiation, i.e. gamma-rays (γ-rays), provides in principle an ideal initiator for emulsion polymerization because of its high degree of penetration (Stannett & Stahel, 1991). The radiation-induced polymerization method offers more benefits as compared to the thermal decomposition of chemical initiators method due to its (gamma-ray) ability to induce polymerization, which can be controlled more easily when the homogenously γ-ray irradiation is penetrating through the sample. The system is independence of temperature and no additional component has been introduced in the system that might influence the reaction (Chen & Zhang, 2007).

There are studies which have reported that the nanogels and microgels (nanoparticle and microparticle) can be synthesized by combination of polymerization and cross-linking process, usually in the emulsion system (e.g., Ravi Kumar *et al*., 2004; Rosiak *et al*., 2003; Ulanski *et al*., 2002). Ulanski and co-workers (1998) reported that the nanogels and microgels produced using the radiation technique are suited for biomedical applications. In more specific, they described that this method or process is free of initiators, monomers and any other additives and it can be used to produce a drug carrier for controlled drug delivery system. Besides that, this method is able to control the size and composition of the microscopic polymer structure through a proper selection of the polymer concentration, type of the irradiation and dose rate (Rosiak *et al*., 2003).

Furthermore, natural polymers, such as vegetable oils, have been used in developing nanoparticles as a carrier for controlled drug delivery. The microemulsion-based plant and vegetable oil formulations have been found promising in a number of drug delivery applications (Corswant *et al*., 1998). In this work, Acrylated Palm Oil (APO) microemulsion mainly contains the water, while modified palm oil and the PF-127 were used to produce the APO nanoparticle. The microemulsion system was chosen to formulate this APO nanoparticle due to its unique characteristic, whereby its dispersed phase consists of small droplets with a diameter in the range of 100-1000 Armstrong (A^o) (Sharma & Shah, 1985). Besides that, miniemulsion system using water as the dispersed phase is a plentiful, nontoxic, environmental friendly and inexpensive system (Wang *et al*., 2007).

Thus, in the present study, the focus of research was to develop nanoparticle of Acrylated Palm Oil (APO) that could sustainably be used as drug carriers through the radiation-induced initiator method. The work includes examining the effects of concentration of polymer and radiation dose on the size, microstructure and the physiochemical structure of nanoparticles.

MATERIALS AND METHODS

Materials

An APO was produced in the Radiation Technology Division, Malaysian Nuclear Agency (Nuclear Malaysia) Bangi, 43000 Kajang, Selangor, Malaysia and PF-127 purchased from Sigma Aldrich was used as a surfactant. Double distilled and deionized water prepared at Nuclear Malaysia was used to prepare the microemulsion.

Preparation of the APO Nanoparticles

A standard microemulsion system consisting of three components [water, oil (APO) and non-ionic surfactant (PF-127)] was developed to formulate the APO nano-droplets. One concentration of PF-127 surfactant at 0.00039M was used to develop the micellar. Then, two volumes of APO (i.e. 0.18% and 1.8%) were added to the micellar system, respectively. The samples were stirred for one hour at 400 rpm using a magnetic stirrer. Then, they were stirred continuously using a high speed mechanical stirrer (Dispermat, VMA-Getzmann GMBH) for at least one hour at 3000 rpm. The vessels were closed tightly using Para film and degassed for 30 minutes using nitrogen gas. After degassing, the vessel was screwed capped immediately. The samples were then irradiated at 0.36, 0.5, 1, 5, 10, 15 and 25 kiloGray (kGy) using gamma irradiation for fabrication of nanoparticles of the cross-linked APO.

Characterization of the Nanoparticles

The samples were ultrafiltered using a disposable polytetrafluoroethylene (PTFE) teflon filter for removing suspended materials or impurity. The filtrates were collected to determine their size. The filtrates were placed in 1 cm quartz cell before the measurement was done. The mean diameter of the samples was determined by photon cross correlation spectroscopy (PCCS) using a dynamic light scattering (Sympatec Nanophox). The wavelength for this PCCS was at 632 nm. Infra-red spectrum was performed using Fourier Transform Infrared (FTIR) spectroscopy (Perkin Elmer). The FTIR spectroscopy was used to characterize the carbon double bond (C=C) crosslinking transformation of the sample. The Perkin Elmer Spectrophotometer was set-up at spectra in the range of 4000 cm^{-1} to 500 cm^{-1}. The dried samples were analyzed using Attenuated Total Reflectance (ATR) method. The Transmission Electron Microscopy (TEM) images were obtained using a Zeiss microscope (JEOL, Japan) and analyzed at the voltage range of 80-120 kilovolt (kV). The dried samples were placed on a copper grid prior to analysis.

RESULT AND DISCUSSIONS

Formation of APO Nanoparticles

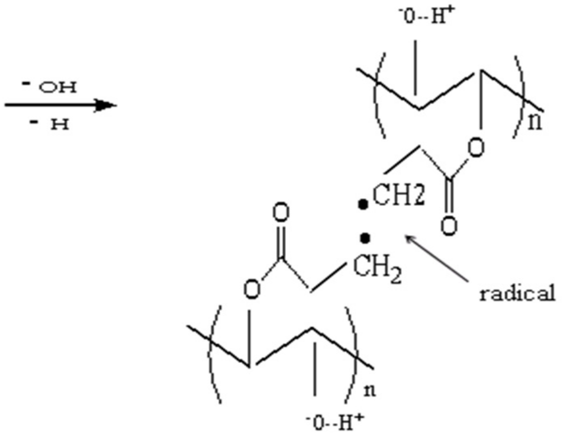
Table 1 tabulated the size of the APO nanoparticle before and after irradiation, as characterized by the dynamic light scattering (DLS). This study found that the size of the APO nanoparticle decreased when increasing the irradiation dose. This was due to the intraparticle crosslinking of the radicals and the hampered diffusion of monomer molecules to the structure (Ulanski & Rosiak, 2004). The intermolecular crosslinking of the nanoparticles was dominant at irradiation process of 1 kGy or lower of the irradiation dose. However, above 1 kGy, the crosslingking reaction of the particles might involve both intermolecular and intramolecular crosslinking proceses. This study revealed that the sample underwent crosslinking, leading to the formation of smaller size of the APO nanoparticles (see Table 1). After the sample had been exposed to the gamma irradiation, the water molecule underwent hydrolysis. As a result, initial reactive intermediates were formed, such as hydroxyl radicals ($^{\bullet}OH$), H-atoms ($H^{\bullet}$) and hydrated electrons (Equation 1). Then, the OH radicals and the H atoms reacted with APO macromolecules by hydrogen abstraction. As a result of this process, a radical was formed on the acrylate's carbon double bond of the APO macromolecule C=C-C- → •C-C-C- (Equation 2). Afterward in the APO molecular structure, these radicals •C-C-C- underwent crosslinking reaction and this resulted in the formation of networking between the APO chains after being subjected to the maximum dose of gamma irradiation (Equation 3). In this study, the maximum dose for the APO nanoparticle to undergo the crosslinking was approximately between 10 to 25 kGy using gamma irradiation. Ulanski and Rosiak (1999) reported that the nanogel dimensions became smaller as compared to the parent (origin) polymer because of the shrinkage of the initial loose and mobile polymer coils into a more tightly bound entities. In this study, the smallest size of the APO particle formation was approximately 98.70 nm at 25 kGy in the 0.18% of the APO/PF-127 system. Besides that, the study also showed that the higher APO content sample produced bigger particle size, as shown in Table 1.

TABLE 1: Size of the PF127/APO nanoparticles upon irradiation

Dose (kGy)	Particle Size, nm	
	0.18% APO	1.8% APO
0	184.74	219.45
0.36	172.94	192.72
0.50	122.29	173.48
1	115.36	132.36
5	114.99	132.35
10	99.37	130.65
15	99.45	133.05
25	98.70	141.80

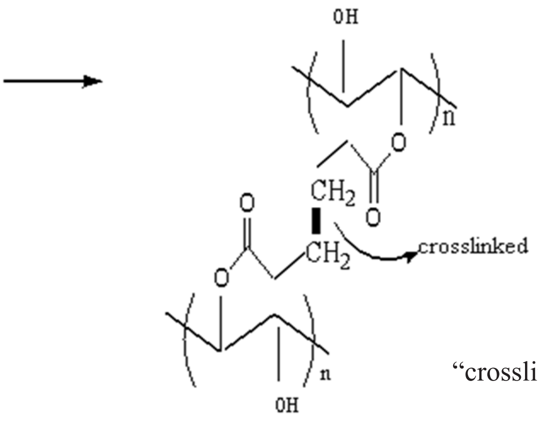
**kGy-kiloGray, nm-nanometer*

$$H_2O \xrightarrow{\gamma} {}^{\bullet}OH,\ H^{\bullet},\ e^-_{aq},\ H^+,\ OH^-,\ H_2O_2,\ H_2$$ [Equation 1]



"radical generation"

[Equation 2]



“crosslinking”

[Equation 3]

Fourier Transform Infra-red (FTIR) Spectra Analysis

Fig.1 shows the spectrum of the APO nanoparticle before and after irradiation. The spectrum clearly showed that the IR peaks of the APO nanoparticle underwent transition schematically from 0 kGy, 1 kGy, until the 25 kGy. As detected by the IR spectrum in Fig.1 (*see* the spectrum before irradiation at 0 kGy), it was demonstrated that the peaks at 2921 -2856 cm^{-1} represented -CH stretching from the PF-127 and the APO mixture, whereby these peaks consequently illustrated the existence of the microemulsion hydrocarbon or the micellar core. Furthermore, the peaks of 3432, 1741, 1638, 1404, 985, 810 and 1282-1243 cm^{-1} represent the APO’s functional groups such as -OH (alcohol), C=O (carbonyl), C=C (acrylate’s carbon-carbon

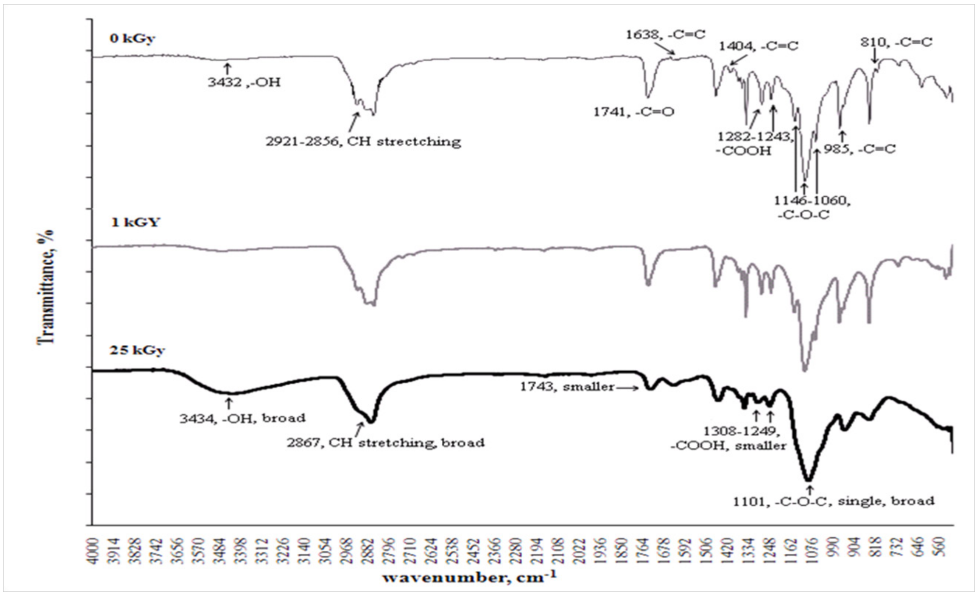
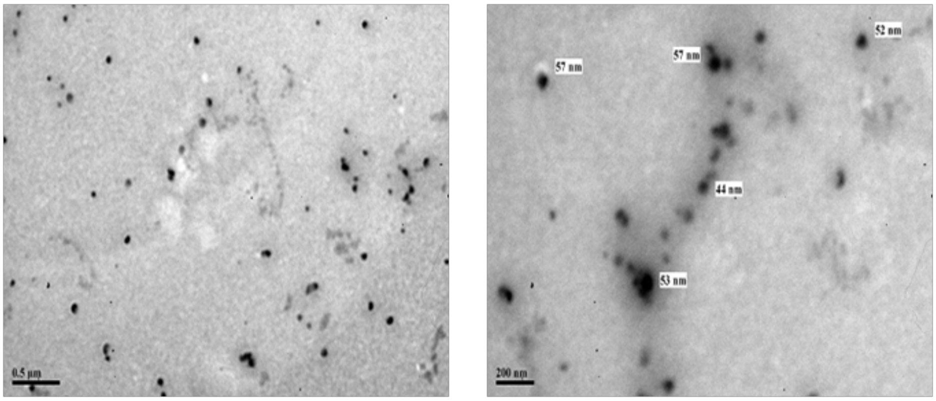


Fig.1: FTIR spectra of the APO/PF127 nanoparticle, before (at 0 kGy) and after irradiation at 1 kGy and 25 kGy, respectively.

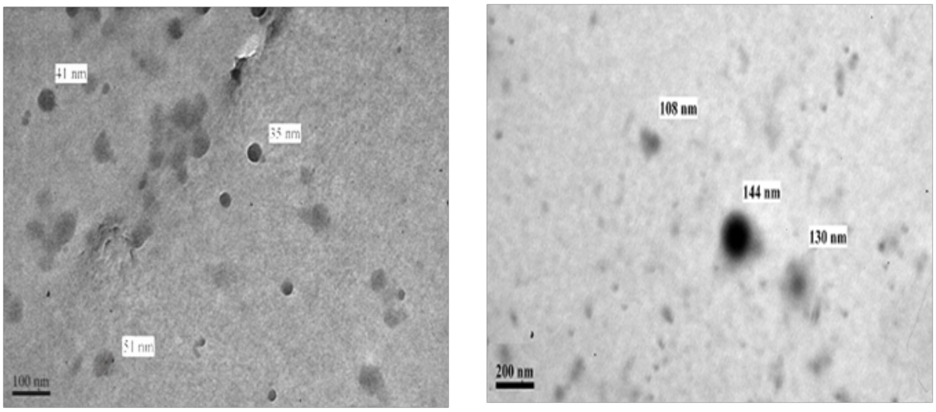
double bond) and COOH (carboxylic). The bands at 1146 to 1060 cm^{-1} were due to the presence of PO (propylene oxide) chains (C-O-C) of hydrocarbon chains of the PF-127.

After irradiation, the peaks slowly underwent transition at 1 kGy (see Fig.1, spectrum at 1 kGy). When the irradiation dose increased to 25kGy, the carbon double bond (C=C) peaks disappeared at 1638, 1404, 985 and 810 cm^{-1}, confirming that the APO nanoparticle was completely crosslinked (see Fig.1, spectrum at 25 kGy). Besides that, the height peak of -OH at 3434 cm^{-1} was increasing and becoming broader due to the increasing amount of APO networking chains. The occurrence of the interaction between the hydrocarbons chains of PO and APO was illustrated by the appearances of the broad and single -CH stretching peaks at 2867 cm^{-1}. Meanwhile, the existence of C-O-C of the PO group was demonstrated by the appearance of the single and broad peak at 1101 cm^{-1}. Furthermore, the C=O and COOH peaks were also shown to be smaller and broader at 1743 cm^{-1} and 1308-1249 cm^{-1}, respectively. This study revealed that the polymerization and the crosslinking process to form the APO nanoparticle seemed to be completed at 25 kGy.



120 kV, magnification: 5000
(a) Before irradiation

120 kV, magnification: 10 000
(b) Before irradiation



80 kV, magnification:20 000
(c) After irradiation at 1kGy

120kV, magnification:10 000
(d) After irradiation at 25kGy

Fig.2: The TEM images of the APO/PF-127 nanoparticles formulated with 1.8% w/v EPOLA in 0.00039 M PF-127, before (*a*,*b* at 0 kGy) and after irradiation (*c* at 1 kGy and *d* at 25 kGy)

Transmission Electron Microscopy (TEM) Images

Fig.2 shows images of the APO nanoparticle before and after irradiation. As illustrated in the figure, the size of the nanoparticle was approximately in the range of 44-57 nm (Fig.2b) for the before irradiation, 35-51 nm (Fig. 2c) and 108-144 nm (Fig.2d) for the after irradiation at 1 and 25 kGy, respectively. The shape of the APO nanoparticle was spherical and its size distribution was not uniform. The main factor of the particle size enlargement after irradiation at 25 kGy (Fig. 2d) was due to the diffusion of the hydrophobic core of PO and APO, in addition to the growth of C=C crosslinked chains in the nanoparticle.

CONCLUSION

This study has shown that the APO nanoparticles were successfully developed by using the radiation-induced initiator method in the microemulsion system. The results obtained revealed that the size of the APO nanoparticle produced in this study was in the nanometer and submicron, which was below 200 nm particle size after irradiation using gamma-rays. The size of the APO nanoparticles depended upon the irradiation doses and the microemulsion formulations.

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REFERENCES

Chen, J., & Zhang, Z. C. (2007). Radiation-induced polymerization of methyl methacrylate in microemulsion with high monomer content. *Journal of European Polymer*, *43*, 1188-1194.

Corswant, C. V., Thorean, P., & Engstrom, S. (1998). Triglyceride-based microemulsion for intravenous administration of sparingly soluble substances. *Journal of Pharmaceutical Sciences*, *87*(2), 200-208.

Ravi Kumar, M. N. V., Sameti, M., Kneuer, C., Lamprecht, A., & Lehr, C. M. (2004). Polymeric Nanoparticles for Drug and Gene Delivery. *Encyclopedia of Nanoscience And Nanotechnology*, *9*, 1-9.

Rosiak, J. M., Janik, I., Kadlubowski, S., Kozicki, M., Kujawa, P., Stasica, P., & Ulanski, P. (2003). Nano-, Micro- And Macroscopic Hydrogels Synthesized By Radiation Technique. *Nuclear Instruments and Methods in Physics Research B*, *208*, 325-330.

Sharma, M. K., & Shah, D. O. (1985). *Macro- and Microemulsions: Theory and Applications*. Washington: American Chemical Society.

Stannett, V. T., & Stahel, E. P. (1991). *Radiation Processing (An Overview in Radiation Processing of Polymers)*. New York: Hanser Publishers.

Ulanski, P., Janik, I., & Rosiak, J. M. (1998). Radiation Formation of Polymeric Nanogels. *Radiation Physics and Chemistry, 52*, 1-6.

Ulanski, P., & Rosiak, J. M. (1999). The use of radiation technique in the synthesis of polymeric nanogels, *Journal of Nuclear Instruments and Methods in Physics Research (B)*, *151*, 356-360.

Ulanski, P., Kadlubowski, S., & Rosiak, J. M. (2002). Synthesis of Poly (acrylic acid) Nanogels by Preparative Pulse Radiolysis. *Radiation Physics and Chemistry, 63*, 533-537.

Ulanski, P., & Rosiak, J. M. (2004). Polymeric Nano/Microgels. *Encyclopedia of Nanoscience and Nanotechnology*, *X*, 1-26.

Wang, S., Wang, X., & Zhang, Z. (2007). Preparation of polystyrene particles with narrow particle size distribution by γ–ray initiated miniemulsion polymerization stabilized by polymeric surfactant. *Journal of European Polymer*, *43*, 178-184.