PALM OIL-BASED POLYESTER NANOPARTICLES
NANO PARTIKEL BERASASKAN MINYAK SAWIT POLIESTER

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Abstract

Development of biodegradable polyester nanoparticles have been extensively explored for use in drug delivery systems. This paper describes the methods utilized to form palm oil-based polyester nanoparticles using gamma radiation grafting technique and describes the obtaining nanoparticles physiochemical properties. The radiation grafting method can be used to obtain palm oil-based polyester nanoparticles with the particle sizes in the range of 60 to 100 nm with a small particle size distribution, which the particle sizes and images can be investigated using dynamic light scattering (DLS) and transmission electron microscopy (TEM). The chemical functional group of nanoparticles can be investigated by Fourier transform infrared **(**FTIR) spectroscopy analysis. This research study can contribute to ensure success in production of promising palm oil-based polyester nanoparticles for use in drug delivery system.

Abstrak

Pembangunan partikel-nano poliester terbiodegradasi untuk digunakan dalam sistem penyampai ubat telah giat dijalankan secara meluas. Kertas ini menerangkan metodologi yang digunakan untuk menghasilkan partikel-nano poliester yang berasaskan minyak sawit menggunakan teknik pencangkukan sinaran gama dan menerangkan sifat fisiko-kimia partikel nano yang dihasilkan. Kaedah pencangkukan sinaran boleh digunakan untuk menghasilkan partikel-nano poliester berasaskan minyak sawit bersaiz dalam lingkungan 60 hingga 100 nm dengan taburan saiz partikel yang kecil, dimana saiz dan imej partikel boleh dikaji menggunakan serakan cahaya dinamik (DLS) dan mikroskopi elektron transmisi (TEM). Kumpulan berfungsi kimia pada partikel nano juga boleh dianalisa menggunakan alat spektroskopi Fourier Transform Infrared (FTIR). Kajian penyelidikan ini boleh menyumbang kepada kejayaan penghasilan partikel-nano poliester berasaskan minyak sawit sebagai sistem penyampai ubat.

Keywords/Kata kunci: palm oil-based nanoparticles, polyester nanoparticles, radiation grafted nanoparticles

INTRODUCTION

The polyester-based nanoparticles led to new biodegradable polymers for controlled delivery of therapeutic drugs (Gentile et al., 2014; Llorens et al., 2013). Polyesters have attracted considerable attention because the chemical properties of these polymers, the ester bonds allow hydrolytic degradation whereby the monomeric components of the polymer can be removed by natural pathways (Gentile et al., 2014). Thus, polyester are considered as biodegradable and biocompatible polymers comparable to many petrochemical-based non-biodegradable polymers. The polyesters have potential application for usage into environmental friendly materials and also in the biomedical fields such as for usage in drug delivery, resorbable surgical sutures and implantable devices (Baharu et al., 2015).

The acrylated palm olein (APOo) and the Polyol is a polyester synthesized from palm olein and oleic acid, respectively (Mahmood et al., 2011). In the last decade, these materials have been extensively developed into radiation curable resins for usage as surface coating, printing inks, adhesive and polyurethane materials (Salih et al., 2015; Salleh et al., 2010). The APOo and the Polyol can be considered as family of promising polymers for developing a drug nanocarrier. In the previous study, Tajau et al. have developed palm oil-based nanoparticles

using the APO, surfactant and aqueous system by a gamma radiation crosslinked technique and the study obtained broad particle size distribution (Tajau et al., 2013).

Hence, this project is aimed to develop a new process using a reversible addition–fragmentation chain transfer (RAFT) polymerization technique by gamma radiation for developing small particle size distribution of palm oil-based polyester nanoparticles. These preliminary study objectives are to synthesis the nanoparticles using an APOo and a Polyol and to characterize the obtained nanoparticles.

METHODOLOGY

Radiation grafting of palm oil-based polyester nanoparticles

The synthesis of the chain transfer agent (CTA), macro-acrylated palm olein (macro-APOo), utilized for the following RAFT (reversible-addition fragmentation chain transfer) polymerizations, was prepared in two different methods. The first method is using the 0.001 M Cetyl trimethyl ammonium bromide (CTAB) solution, the APOo and the dibenzyltritiocarbonate (DBTC) as the radical initiator whereas the second method is using the 0.001 M CTAB solution, the APOo and the DBTC in the presence of ethyl acetate solution as the radical initiator. All the mixtures were irradiating using the gamma radiation at 500 gray.

The RAFT polymerization of palm oil-based polyester nanoparticle was conducted using the macro-APOo solution, the palm oil-based polyester (the APOo or the polyol) and the DBTC. Another set of sample was prepared in the presence of ethyl acetate solution. The samples were slowly stirred for 1 hr and 24 hrs using a magnetic stirrer, respectively, before continuously stirs using a high speed disperser at 30000 rpm for an hour. All RAFT polymerizations were carried under a nitrogen atmosphere and were exposing to a gamma radiation at 10 kilogray doses.

The resulting nanoparticle solutions were collected by filtration through a 0.20 μm membrane and dried using lyophilisation technique.

Characterization of palm oil-based polyester nanoparticles

The particle size of the nanoparticles was measured using dynamic light scattering (Nanophox). The images of the nanoparticles were measured using TEM. The chemical functional group of the grafted nanoparticle were analysed using FTIR spectroscopy.

RESULTS AND DISCUSSION

Particle Size

Table 1 shows the mean diameters of macro-APOo that were synthesized using gamma radiation whereas Table 2 shows the mean diameters for palm oil-based polyester nanoparticles which were synthesized by gamma irradiation. It can be clearly seen that a nanoparticle produced using Method 1 (without ethyl acetate solution) is rather small for this synthesis parameter for gamma irradiation which is less than 90 nm. Especially for Method 1 there is a slightly different in particle size due to the duration of stirring of the samples for 1 hr and 24 hrs. Overall, the APOo-grafted-Polyol nanoparticle which is stirs for 1 hrs results a smaller mean diameter at 79.41 nm compared to the others sample.

Table 1. The mean diameters of macro-APOo.

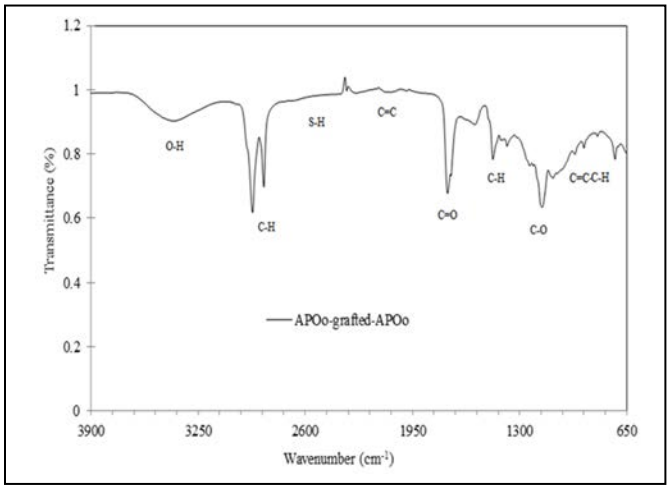
Sample	Macro-APOo
Method 1	78.06 nm (std.dev: 3.23)
Method 2	74.52 nm (std.dev: 4.55)

Table 2. The mean diameters of palm oil-based polyester nanoparticles.

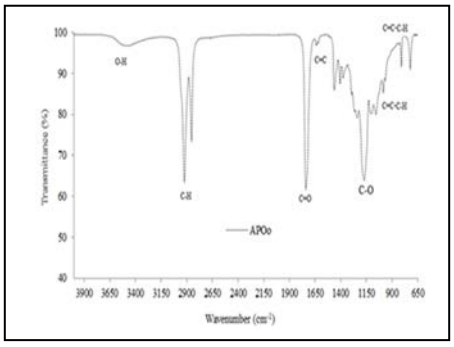
Sample	Palm oil-based polyester nanoparticles, nm			
	Using a Macro-APOo from Method 1		Using a Macro-APOo from Method 2	
	1hrs	24 hrs	1hrs	24 hrs
APOo-grafted-APOo	85.67 nm (std.dev: 0.48)	82.08 nm (std.dev: 2.10)	87.6 nm (std.dev: 1.95)	715.25 nm (std.dev: 12.12)
APOo-grafted-Polyol	79.41 nm (std.dev: 0.46)	82.92 nm (std.dev: 2.65)	99.04 nm (std.dev: 0.56)	91.82 nm (std.dev: 1.03)

FTIR Spectroscopy

The FTIR spectroscopy can be used for the characterization of the conversion of polymer. In this study, the intensity of C=C peaks of the monomer would be a good indicator of the conversion which the polymerization takes place by breaking of alkene C-H bend (C=C bonds) followed by interconnection of the monomers. In case of APOo-grafted-APOo nanoparticles the C=C peaks can be observed at 1005 cm^{-1} to 730 cm^{-1}, and these peaks really decrease after irradiation (Fig. 1a) compared to the alkene C=C bonds of neat APOo at Fig.1b. The C=C bands of neat APOo in Fig. 1b shows the peak intensity were higher before the sample is irradiated. The low intensity of the alkenes C-H bend peaks between 1005 cm^{-1} to 730 cm^{-1} in APOo-grafted-APOo nanoparticles (Fig. 1) may be attributed to grafting between the macro-APOo and the APOo after irradiation. Furthermore, the bands at 1176 cm^{-1} is assigned to ester group (C-O) and strong peak at 3446 cm-1 is corresponding to alcohol of O-H group of nanoparticles (Fig. 1a). The low intensity peak at 2535 cm^{-1} is assigned to S-H of thiols in nanoparticle (Fig. 1).



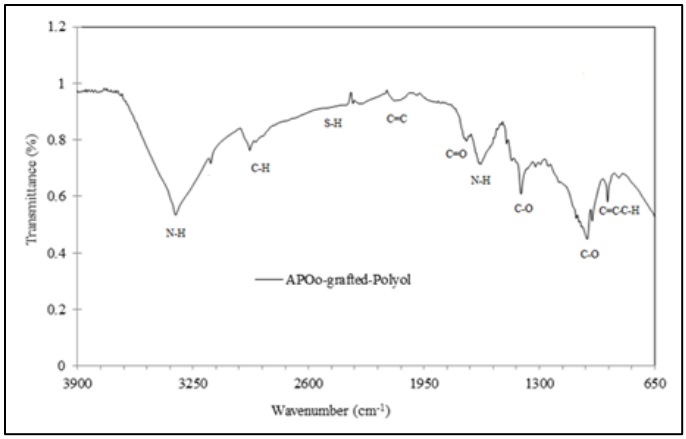
(a) APOo-grafted-APOo nanoparticles.



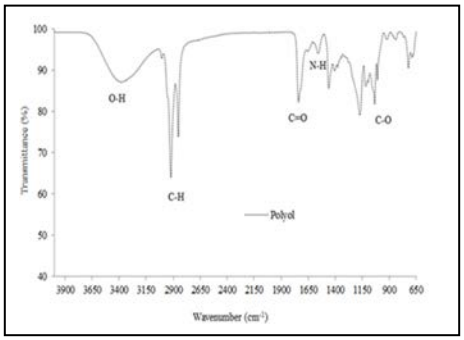
(b) Neat APOo.

Figure 1. FTIR spectra of (a) irradiated APOo-grafted-APOo nanoparticles at 10 kGy and (b) neat APOo.

The FTIR spectra of the APOo-grafted-Polyol nanoparticles (Fig. 2a) show the chemical characteristic peaks of the nanoparticle compared to the neat APOo (Fig. 1b) and the neat Polyol (Fig. 2b). The high intensity of the two bands for N-H stretch peaks at 3359 cm^{-1} and the alkene CH bend (C=C) peaks between 1021 cm^{-1} to 888 cm^{-1} in APOo-grafted-Polyol nanoparticles (Fig. 1) may be attributed to polymerization between the macro-APOo and the Polyol after irradiation. The low intensity peak at 2542 cm^{-1} is assigned to S-H of thiols in nanoparticle (Fig. 1) which is might attributed to the grafting of the macro-APOo and the Polyol.



(a) APOo-grafted-Polyol nanoparticles.



(b) Neat Polyol.

Figure 2. FTIR spectra of (a) irradiated APOo-grafted-Polyol nanoparticles at 10 kGy and (b) neat Polyol.

TEM Image

TEM micrograph of APOo-grafted-APOo nanoparticles are shown in Fig. 3. It is obvious that these APOo-grafted-APOo nanoparticles at nanoscale levels. The detailed on the nanoparticle images will be further discussed in future studies.

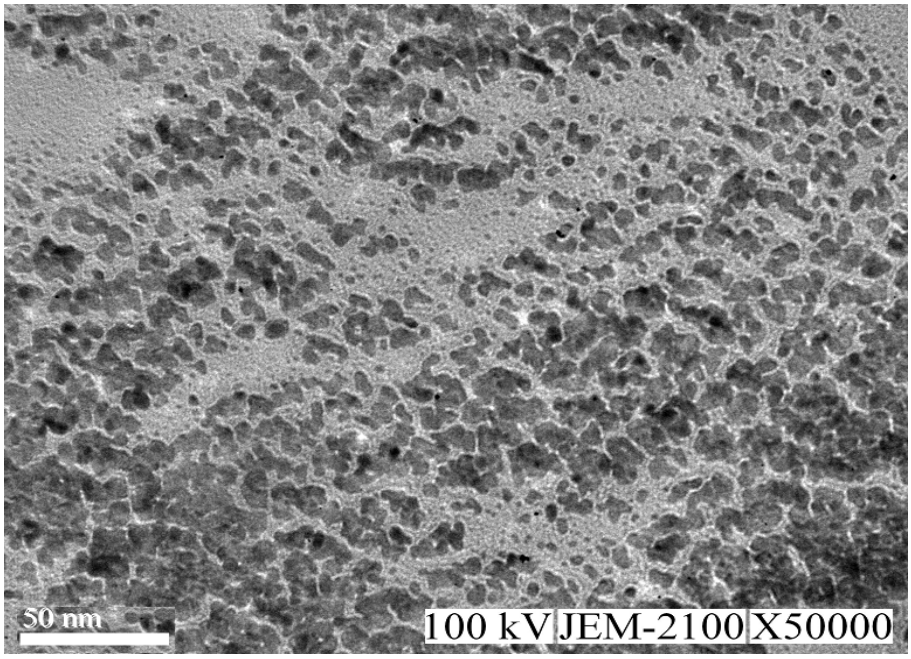


Figure 3. TEM images of APOo-grafted-APOo nanoparticles.

CONCLUSION

Our first preliminary results evidenced that this palm oil-based polyester (the APOo and the Polyol) as a promising candidate for use in developing nanoparticles. The RAFT technique and the gamma radiation processes can be considered as potential methods to synthesis the palm oil-based polyester nanoparticles with a small particle size distribution.

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