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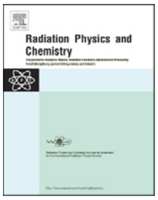

Emulsion graft polymerization of 4-chloromethylstyrene on kenaf fiber by pre-irradiation method

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HIGHLIGHTS

- ▸ The stability of 4-chlorometylsyrene (CMS) emulsion was studied by static light scattering and optical microscope.
- ▸ Different micelle size was obtained by adjusting the ratio between CMS and Tween 20.
- ▸ Effect of micelle size on radiation induced graft polymerization onto kenaf fiber was evaluated.
- ▸ Microscope observations of the CMS emulsion revealed that some of the micelles were of a multiple type.
- ▸ Mechanism during radiation induced graft polymerization was predicted.

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ABSTRACT

The stability of micelle size in 3% 4-chloromethylstyrene (CMS), 0.3% Tween 20 in water emulsion over time was studied using a static light scattering. It was found that the micelle diameter decreased with storage time and temperature. The influence of micelle size over time was then explored by adjusting the ratio of CMS to Tween 20 (10:1, 10:2, 10:4) at CMS concentration of 0.2–5.0%. It was found that the increase in average micelle diameter resulted in a decreased in the stability of CMS emulsion. Graft polymerization of CMS on kenaf fiber was carried out in emulsion with 350 nm micelle at various CMS concentrations at a dose of 150 kGy. It was found that the degree of grafting (Dg) was strongly dependent on the monomer concentration and time. However, the increase in micelles diameter from 250 nm to 500 nm resulted in the increased in Dg from 3% to 153%. This extraordinary result led us to investigate the micelle size distributions of CMS emulsion during graft polymerization. It was found that the diameter of micelle decreased rapidly to 100 nm within 2 h. It was discovered from digital photomicrography the existence of multiple emulsions in the CMS emulsion. It was proposed that the enhancement of grafting yield is governed by emulsion breakdown mechanisms through radical effect during radiation induced graft polymerization.

1. Introduction

A functional monomer, 4-chloromethylstyrene (CMS), is one of the most available precursor monomers for synthesis of metal adsorbents. Grafting of CMS onto the polymeric fiber can manufacture the anionic exchange absorbents containing trimethylamine groups, which are promising in applications such as in electrodialysis and extraction of biodiesel from vegetable oils (Sata et al., 1996; Ueki et al., 2011). A great variety of compounds can be formed by nucleophilic substitutions (Babazadeh, 2006) at the position of benzylic chlorine. Hamabe et al. (2009) developed bifunctional phosfonate material derived from CMS grafted polyolefine fibers for metal ion adsorbent. Fibers having graft chain of chloromethylstyrene modified by trimetylamine can chelate some kinds of metal ions such as Pb(II), Cr(VII) and Mn(VII) effectively (Zhang et al., 2008; Jyo et al., 2001).

The grafting of CMS is generally conducted in organic solvents such as benzene and toluene (Herman et al., 2003; Jyo et al., 2001; Tanaka, 1999) owing to poor solubility of CMS in the water phase. From the perspective of green sustainable chemistry, organic solvent-free method is strongly required. Wada et al. (2008) found that the water-based or so-called emulsion graft polymerization of vinyl acetate enhanced the value of grafting degree 100 times higher than that in organic solvent such as methanol. In this case, the most likely mechanism is governed by diffusion of monomer micelles onto trunk polymer (Seko et al., 2007, 2010).

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These studies suggest that micelles size play a major effect on increment of grafting yield.

Recently, we found CMS emulsified by surfactant of Tween 20 was grafted on nonwoven polyethylene (NWPE) fabric (Ueki et al., 2011). However, relationship between micelle size and grafting yield is not clarified. In the present study, we investigate the influence of the micelle size on grafting yield using fiber as a trunk polymer. First, we clarify the effect of storage time and Tween 20 ratio to CMS on micelle size and stability. Then, distribution of micelle size during the grafting reaction was observed. Finally, the promising mechanism in the emulsion graft polymerization of CMS is discussed.

2. Experimental

2.1. Materials

CMS was purchased from Wako Chemical Co., Ltd., Japan. It was purified by passing through MP Alumina B-Super I and methanol (99%). A nonionic surfactant, Tween 20, used as an emulsifier was obtained from Kanto Chemical Co., Inc. (Tokyo, Japan). Deionized water with a Milli-Q deionization system (Nihon Millipore K.K., Tokyo, Japan) was used directly for the preparation of the emulsion solution. Kenaf fiber obtained from Lembaga Kenaf dan Tembakau Malaysia (LKTM) was used as a trunk polymer for radiation induced graft polymerization. Prior to use, kenaf was delignified by acidic chlorite solution modified from the method used by Mohamed et al. (in press).

2.2. Preparation of emulsion

CMS emulsion was prepared by CMS into Tween 20 aqueous solution in the concentration from 0.02% to 2.0% until the concentration of CMS reached 5.0%. This emulsion was stirred at room temperature with magnetic stirrer at 300 rpm for 10 min followed by stirring with high speed homogenizer (Ultra-turrax T 25, IKA Labortechnik, Germany) at 6500 rpm for 18 min. Emulsion was stored in screw capped glass tube and placed in temperature ranged from 15 to 40 °C to study the change in micelles diameter up to 48 h.

2.3. Emulsion analysis

The analysis of micelles diameter was performed using static light scattering (FPAR-1000, Photal Otsuka Electronics Co., Ltd., Japan) at 20 °C. The appearance of micelles was also examined by monitoring the emulsions using an optical microscope (VHX-1000, Keyence VH-Z450) with 3000 × magnification.

2.4. Radiation induced graft polymerization

Polypropylene zipper bag containing 400 mg of dried delignified kenaf was purged with nitrogen. It was irradiated with electron beam of 150 kGy at energy of 2 MeV and 3 mA at −20 °C. The irradiated fiber was immersed in 100 ml CMS emulsion previously deaerated with nitrogen. The grafting reaction was then allowed to react for 24 h at 30 °C in water bath. After the reaction, the grafted kenaf was recovered from the emulsion and washed repeatedly with water followed by methanol to remove left monomer. The weight of the CMS grafted kenaf was determined after overnight dried under reduced pressure at 30 °C. The degree of grafting (Dg) and CMS consumption were calculated according to the following equations:

$$\mathrm{Dg}\ (\%) = \left[\frac{W_1 - W_0}{W_0}\right] \times 100$$

$$\text{CMS consumption}\ (\%) = \left(\frac{W_1 - W_0}{W_2}\right) x100$$

In the equations, W_0 is the initial weights of kenaf, W_1 is the weight of kenaf after grafting and W_2 is the weight of CMS in emulsion.

3. Results and discussion

The stability of CMS micelle was first studied by mixing 2.0% CMS, 0.3% Tween 20 and 97.7% water. The size changes of 350 nm micelle stored at 15–40 °C up to 24 h is presented in Fig. 1. It is obvious that the micelles diameter changes marginally with the increasing storage time. It also evidenced from the figure that the decrease in the diameter is strongly temperature dependence. At 15 °C, the diameter decrease slowly from 350 nm to 339 nm (at 4 h), 282 nm (at 24 h) and 283 nm (at 48 h). A continuous decrease in diameter is also observed at both 20 and 30 °C with smallest diameter reached 224 nm and 174 nm at 48 h respectively. At 40 °C, the diameter decrease drastically to 153 nm within 1 h and starts to increase appreciably until it level off to 400 nm after 4 h. The rapid decrease in micelles diameter is believed to result from the increase in monomer solubility at higher temperatures (Antonietti and Landfester, 2002), which might increase the Oswald ripening effect. This resulted in the instability of the emulsion, where the smaller micelles will disappear by immigration to larger micelles through a continuous phase (Noor El-Din, 2011) as observed at 40 °C. The absence of micelles growth at temperature from 15 to 30 °C, suggests that the micelles coalescence is weakened at lower temperature. Therefore, the experiment indicates that the emulsions are stable at temperature below 40 °C regardless to effect of storage time on micelles diameter.

In order to determine the effect of time on micelle size, a series of emulsions with different micelle size was prepared by mixing the CMS and Tween 20 in deionized water at a certain ratios (10:4, 10:2 and 10:1) and a fixed CMS concentrations of 0.2, 0.5, 1.0, 2.0 and 5% CMS. It was found that at 10:4, 10:2 and 10:1, the micelle diameters were 250, 350 and 500 nm respectively. The resulting emulsions having different micelle diameters stored at 30 °C up to 48 h are presented in Fig. 2. It was found that for emulsions with 0.5–5.0% CMS, the diameter of 250 nm micelle can be controlled up to 48 h. However, in the emulsion with 0.2%

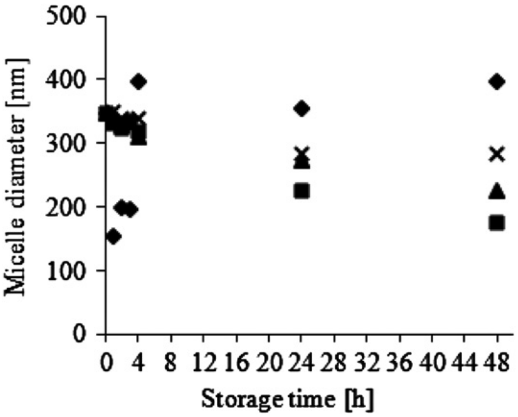

Fig. 1. Effect of temperature on the change of micelle diameter as a function of storage time at [X]15 °C, [▲] 20 °C, [■]30 °C and [◆] 40 °C.