

Photografting of Methacrylic Acid Onto Hydroxyapatite Particles Surfaces

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Received 24 July 2008; accepted 15 August 2009

DOI 10.1002/app.31307

Published online 7 October 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The unsaturated functional groups (C=C) were introduced onto hydroxyapatite (HAP) particles surfaces by esterification reaction between hydroxyl groups on the HAP surface and methacrylic acid (MAA). Then, graft polymerization of MAA onto the esterified HAP particles surfaces was carried out by ultraviolet light (UV) initiation. The structure of the surface-esterified and grafted HAP was studied by ESCA, FTIR, Scanning Electron microscopy, laser particle sizes analyze, esterification, and graft degrees tests. The results show that poly(methyl acrylic acid) (PMAA) is successfully inserted onto HAP particles surfaces by covalent bond linkage. The esterification degree

between MAA and HAP particles increases with reaction temperature and time, and tends to level off at about 6 h under 90°C. The graft degree of MAA onto HAP particles with 1.14% esterification degree and its average particle sizes increase with UV initiation polymerization time, and to reach a maximum at 25 min under 40°C, then decrease as irradiation time further increases. The surfaces of the grafted HAP particles become rough and loose. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 2156–2161, 2010

Key words: surface graft; UV-induced; hydroxyapatite; methacrylic acid

INTRODUCTION

The chemical components of hydroxyapatite [HAP: $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$] are similar to the mineral components of bones and hard tissues in mammals. HAP is bioactive, and can support bone ingrowth, osseointegration in orthopedic and dental applications. It has been considered as the most promising materials for hard tissues replacements.^{1–6} But its low toughness is one of the most serious barriers for its wider applications as load-bearing replacement materials. As Bonfield put forward that bioactive HAP composites based on polymer matrix could be used as bone replacement materials in 1980s,⁷ various HAP composites have gained increasing attentions.^{8–15} The resulting polymer matrix composites can offer HAP both toughness and processing properties, while polymer matrix is endowed with biological activity. However, the interface interaction between HAP and most polymer matrices is poor, that will result in poor properties of HAP composites based on polymer matrix. Therefore, how to improve the interface interaction between HAP and

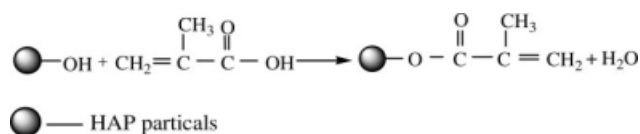
polymer matrix is a key factor to prepare a high performance HAP composites. Many studies have focused on improving the surface compatibility between the HAP and polymer matrix.^{8–15} In our previous article,¹⁶ we briefly explored a surface modification method for HAP particles through the surface-esterification reaction and then photografting. In this study, an effective surface modification method for HAP had been developed in detail through surface photografting. Firstly, carbon-carbon unsaturated double bond functional groups (C=C) were covalently inserted onto the HAP surface by esterification reaction with methacrylic acid (MAA), subsequently, polymerization reaction of MAA onto the surface-esterified HAP was initiated through UV light. Effect of reaction conditions on the esterification degrees and the graft degrees, reaction mechanisms and the surface structures of HAP modified by this way were studied.

EXPERIMENTAL

Materials

HAP was purchased from Guilin Hongxing Biotechnology (China). 2, 2-Dimethoxy-2-phenylacetophenone used as photosensitizer was purchased from Zhenjiang Jianxing Chemical (China). MAA

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Scheme 1 Esterification of HAP surface with methacrylic acid.

monomer was purified by distillation under reduced pressure before use. All of the water used was deionized.

Preparation of surface-esterified HAP

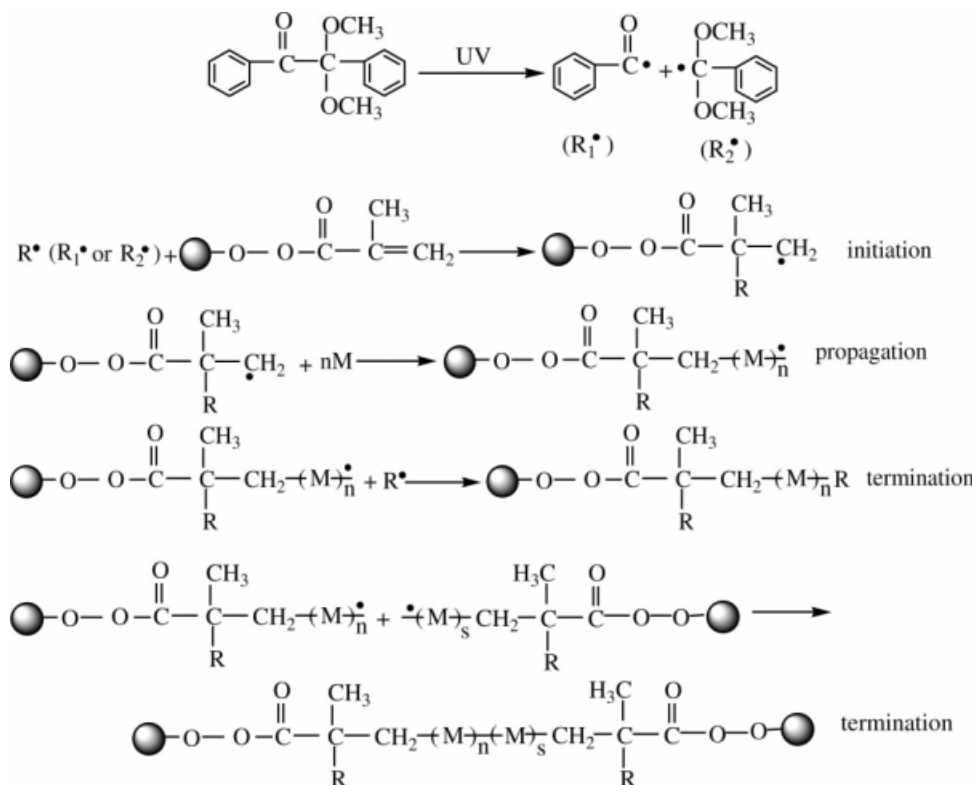
HAP (15.010 g), benzene (75 mL), *p*-benzenediol (0.210 g) (as inhibitor), toluene-*p*-sulfonic acid (1.065 g) (as catalyzer), and 25 mL MAA were added into a 250 mL flask assembled with mechanical agitator (stirring rate: 200 rpm), centigrade thermometer and reflux condenser. The esterification reaction was taken under stirring at a set temperature for a given time. The filtrated part of reaction production thoroughly washed two more times with hot distilled water, then extracted with chloroform for 24 h in a Soxhlet apparatus to remove the residual MAA, its homopolymer poly(methyl acrylic acid) (PMAA) and other impurities, at last dried to a constant

weight at 45°C under vacuum to obtain the purified esterified HAP (EHAP).

The esterification reaction can be described as Scheme 1.

Polymerization of MAA onto EHAP or pure HAP initiated by UV light to prepare GEHAP or GHAP

MAA monomers (0.3 g) and photosensitizers (0.02 g) were dissolved in ethanol (weight ratio of MAA/ethanol: 6/100) to form reaction solution, then homogeneously mixed with 2.0 g the prepared EHAP or pure HAP. The mixture was poured into a sealed glass vessel, and then placed into a UV irradiation device designed in our laboratory.¹⁷ The device used was the same one as in Ref¹⁶ and a sealed glass vessel, in which the samples were added for photografting was installed into an oven, so irradiation reaction temperature could be controlled by oven. The Ga-I UV lamp used with a power of 500 W was manufactured by Chengdu Lamp Company, China. After graft polymerization reaction carried out for a given time by UV irradiation, the filtrated part of reaction production thoroughly washed two more times with hot distilled water, then extracted with chloroform for 24 h in a Soxhlet apparatus to remove the residual MAA, its homopolymer (PMAA), and other impurities, at last dried



Scheme 2 Photografting polymerization of methacrylic acid on HAP surface.

to a constant weight at 45°C under vacuum to obtain the purified GEHAP or GHAP.

The photografting reactions take place as free radical polymerization and can be described as Scheme 2.

CHARACTERIZATIONS

The esterification degree measurement of EHAP

The esterification degree of MAA onto the HAP surfaces was calculated by the following eq. (1):

$$E = \frac{W_2 - W_1}{W_1} \times 100\% \quad (1)$$

W_1 – the weights of HAP before esterification, (g)

W_2 – the weights of HAP after esterification, (g)

E – the esterification degree

The graft degree measurement of GEHAP

Certain amount of GEHAP were dipped into an ethanol/NaOH mixture solution in a flask assembled with reflux condenser at boiling temperature of ethanol for 3 h to neutralize the grafted MAA, and then cooled to ambient temperature. Phenolphthalein was added as an indicator, and the solution mixture turned red. HCl solution was drip fed to neutralize the residual NaOH until the solution became leuco. The graft degree of MAA onto the GEHAP surface was calculated by the following eq. (2):

$$G = \frac{(V_{\text{NaOH}} \times C_{\text{NaOH}} - V_{\text{HCl}} \times C_{\text{HCl}}) \times 0.001 \times M_{\text{AA}}}{m} \times 100\% \quad (2)$$

m – the original weight of SEHAP, g

M_{AA} – the molecular weight of AA, g

$V_{\text{NaOH}}, V_{\text{HCl}}$ – the volumes of NaOH and HCl solutions, mL

$C_{\text{NaOH}}, C_{\text{HCl}}$ – the concentrations, of NaOH and HCl solutions, mol/L

FTIR spectrum analysis

FTIR spectra were taken as a KBr pellets with Nicolet FTIR 20SXB infrared spectrometer made in America.

ESCA characterization

ESCA spectra were obtained on a Kratos XSAM 800 spectrometer, using a monochromatic AlK_{α} phone source.

SEM observation

The morphologies of the particles surfaces were observed by a scanning electron microscope (SEM) using JSM-5900LV made in Japan. All surfaces were coated with a thin layer of silver before scanning electron microscopy (SEM) examination.

Particle size and its distribution measurements

Particle size and its distribution measurement were tested by Laser Particle Size Analyzer LS-POPIII, OMEC Sci. & Tech., (Zhuhai, China).

RESULTS AND DISCUSSION

Effect of reaction time on the esterification degree at different temperature

Figure 1 shows that the esterification degree of MAA onto the HAP surface initially increases with the reaction time, and then tends to level off. When the reaction temperature is 90°C, the esterification degree tends to level off at about 6 h. Reaction temperature elevation is beneficial for esterification reaction.

Effect of irradiation time on the graft degree of MAA onto EHAP at different esterification degree

From Figure 2, it can be seen that graft degree increases with irradiation time. At the same irradiation time, the graft degree on EHAP increases with esterification degree. This may be due to the fact that the higher esterification degree can insert more carbon-carbon double bonds (C=C) onto HAP

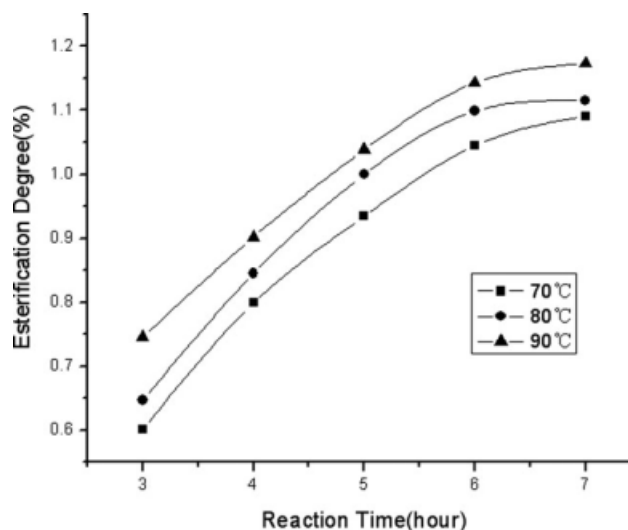


Figure 1 Effect of reaction time on the esterification degree of MAA onto HAP surface at different temperature.

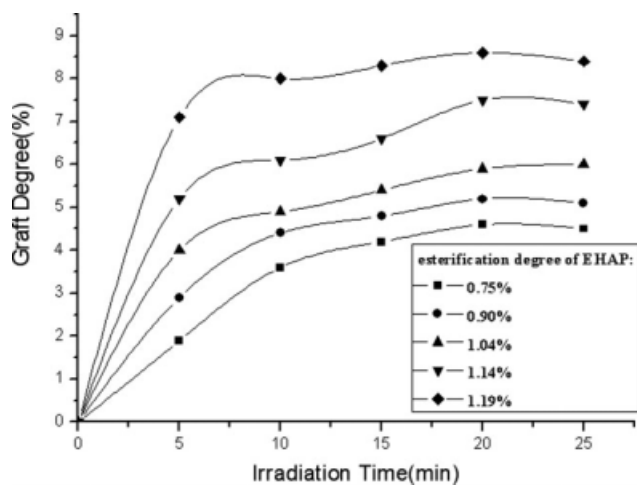


Figure 2 Effect of irradiation time on graft degree at different esterification degree (reaction temperature: 25°C).

surfaces, namely active sites increase during UV-induced graft polymerization.

Figure 3 shows that the graft degree of MAA onto EHAP initially increases with irradiation time and to reach a maximum at 25 min under irradiation temperature 40°C, then decreases as irradiation time further increases. This may be due to the degradation of the grafted PMAA onto the EHAP surface under long time exposure to UV irradiation.

ESCA results

ESCA results of pure HAP and EHAP had been reported in our previous article.¹⁶ It had been certified that esterification reaction took place between the hydroxyl groups on the HAP surface and MAA (scheme 1). Figure 4 shows that the contents of car-

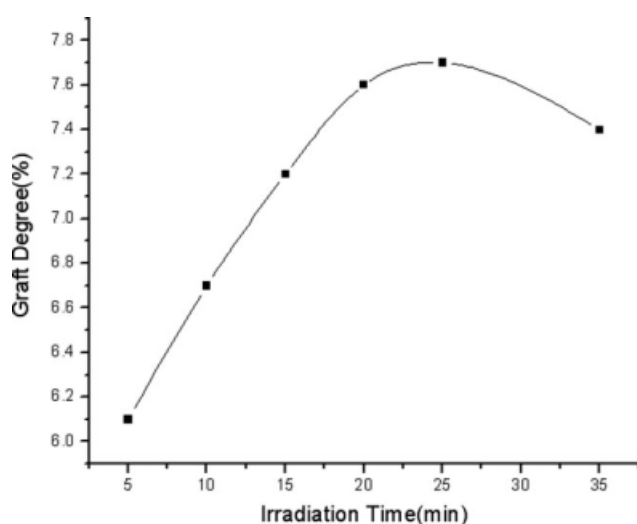


Figure 3 Effect of irradiation time on graft degree of MAA onto EHAP in MAA ethanol solution (irradiation temperature: 40°C, weight ratio of MAA/ethanol: 6/94, esterification degree: 1.14%).

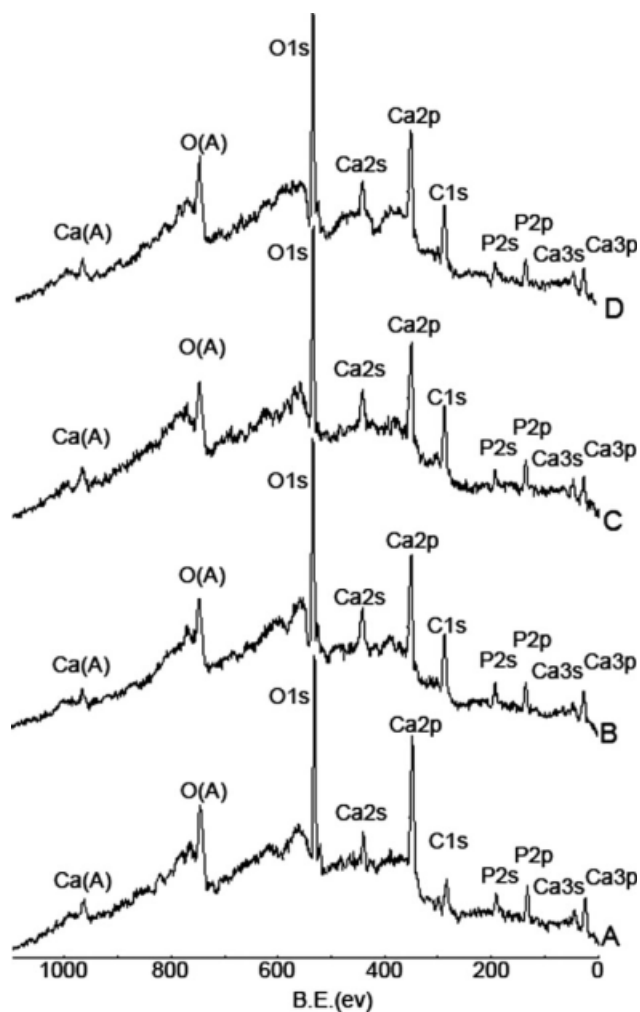


Figure 4 ESCA spectra of GEHAP with different irradiation time A: 5 min B: 20 min C: 25 min D: 35 min (irradiation temperature: 40°C, esterification degree: 1.14%).

bon (C) element on the EHAP surface increase with irradiation time and reach a maximum at 25 min because of the UV initiated polymerization of MAA onto the EHAP surface, and then decrease as further irradiation time increase, which is consistent to the results of the graft degree test shown earlier. On contrary, we can also see that the contents of Ca element initially decrease with irradiation time, respectively, and reach to a minimum at 25 min, and then increase with further irradiation time increase. These results confirm that MAA can be graft-polymerized onto the EHAP surface.

FTIR spectra

In our previous study, two new characteristic peaks at $\sim 2950\text{ cm}^{-1}$ and 1710 cm^{-1} in FTIR spectra of EHAP assigning to C—H and C=O groups can be observed respectively, while none these two peaks can be detected for HAP.¹⁶ From FTIR spectra of EHAP polymerized with MAA monomer [Fig. 5(B–G)]

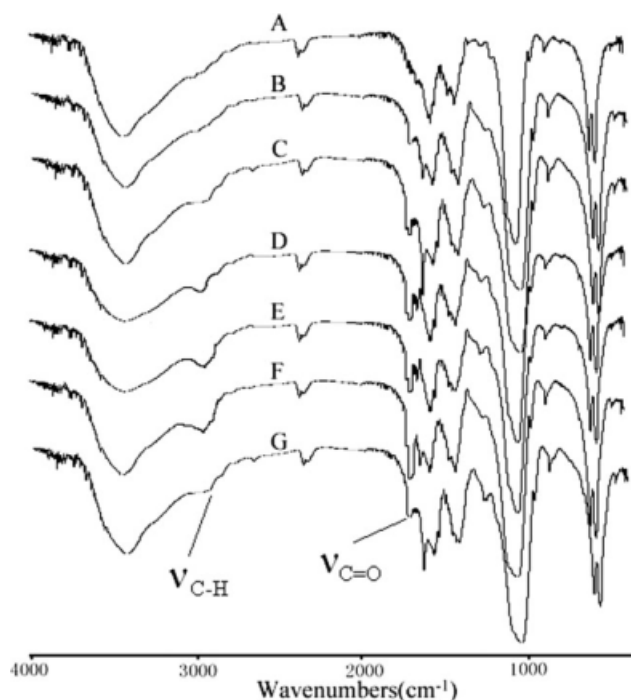


Figure 5 FTIR spectra of GHAP (A) and GEHAP (B–G) polymerized with MAA monomer with UV light different irradiation time A: 25 min B: 5 min C: 10 min D: 15 min E: 20 min F: 25 min G: 35 min (irradiation temperature: 40°C, esterification degree: 1.14%).

it can be seen that there are two characteristic peaks at $\sim 2950\text{ cm}^{-1}$ and 1710 cm^{-1} , and their peak areas increase with irradiation time from 5 min to 25 min,

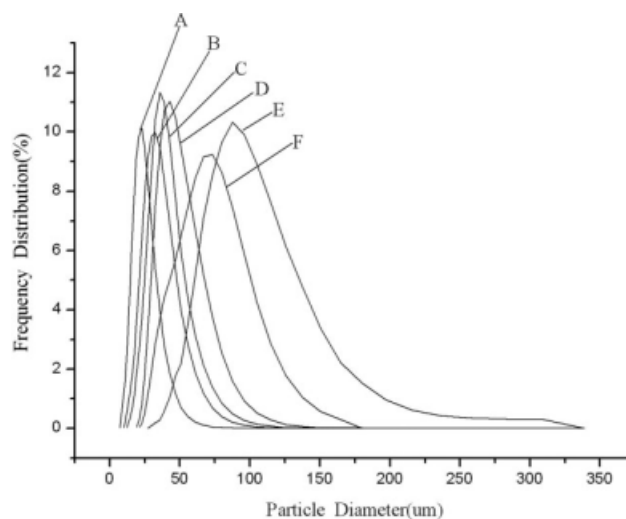


Figure 6 Particle diameter distribute curves of GEHAP at different irradiation polymerization time A: pure HAP B: 5 min C: 10 min D: 15 min E: 25 min F: 35 min (for B–F polymerization temperature: 40°C, esterification degree: 1.14%).

then decrease at irradiation time of 35 min, showing that the carbon-carbon unsaturated $\text{C}=\text{C}$ groups introduced onto the HAP particles by esterification reaction process take part in polymerization reaction with MAA monomer initiated by UV light. So PMAA were formed and covered onto the EHAP surface by chemical bonds linkage (Scheme 2), which can not be removed by purification. However, on the FTIR spectra of GHAP [Fig. 5(A)], only a very tiny peak at

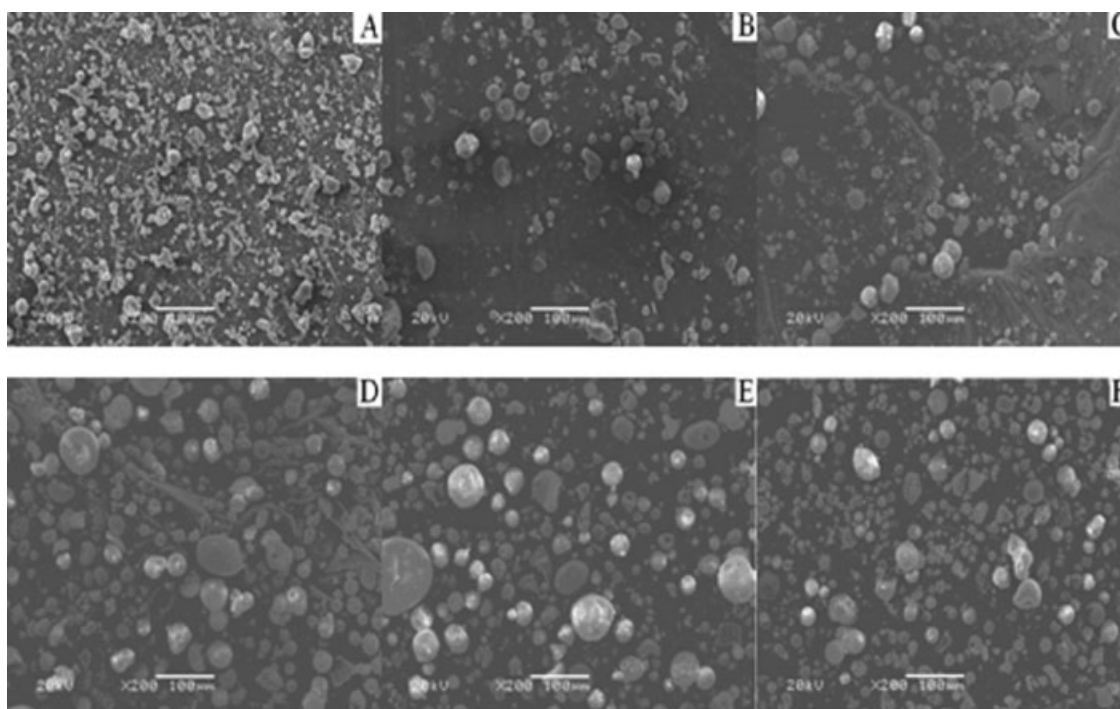


Figure 7 SEM photographs of GEHAP at different irradiation polymerization time A: pure HAP B: 5 min C: 10 min D: 15 min E: 25 min F: 35 min (for B–F polymerization temperature: 40°C, esterification degree: 1.14%).

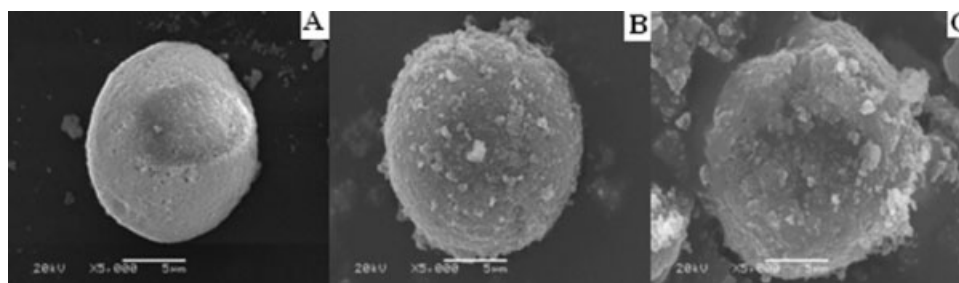


Figure 8 SEM photographs A: pure HAP B: 10 min for GEHAP C: 25 min for GEHAP (for B and C polymerization temperature: 40°C, esterification degree: 1.14%).

$\sim 1710\text{ cm}^{-1}$ can be observed as compared with that of Figure 5(F) with the same photopolymerization conditions due to the fact that almost all MAA monomers form homopolymer under UV irradiation and noncovalently coated with PMAA onto HAP. All of PMAA homopolymer can be removed away during purification, but very small amount of MAA or PMAA may take esterification reaction with $-\text{OH}$ groups on the surface of HAP, so very tiny peak at $\sim 1710\text{ cm}^{-1}$ still can be observed on the FTIR spectra [Fig. 5(A)].

Particle size analysis

From Figures 6 and 7, it can be seen that average particle sizes of GEHAP are all bigger than that of HAP and increase with irradiation polymerization time from 5 to 25min, then decreases at irradiation time of 35min, corresponding with the test results mentioned earlier.

From Figure 8(A–C), we can see the surface of HAP particle is very smooth [Fig. 8(A)], the GEHAP particle surface becomes rough [Fig. 8(B)], and further rougher and looser with polymerization time [Fig. 8(C)] due to the fact that some MAA monomers have been polymerized onto the particle surface to form a graft layer.

CONCLUSIONS

The surface of HAP esterified with MAA can graftly polymerize with MAA in an ethanol solution initiated by UV light. The PMAA polymers prepared are chemically bonded with HAP surface and can not be removed by hot distilled water and chloroform. The

graft degree of MAA onto the HAP esterified with MAA is increased with esterification degree and UV light irradiation time within 25 min. As reaction time increase further, the graft degree of PMAA onto HAP decreases due to the fact that the graft layer of PMAA on the surface degrades. After photografting with MAA, HAP size increases, its surface becomes rough and loose.

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