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Preparation of alginate-polymethacrylate hybrid material by radical polymerization of cationic methacrylate monomer in the presence of sodium alginate

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Abstract

An alginate-polymethacrylate hybrid material was prepared by radical polymerization of a cationic methacrylate monomer, i.e. 2-aminoethyl methacrylate hydrochloride in the presence of sodium alginate in water. The insoluble material was formed with progress of the polymerization. The structure of the product was confirmed by the IR spectrum and elemental analysis, as well as the acid hydrolysis experiment to be composed of alginate and polymethacrylate. The TG and DSC data of product were different from those of a mixture of sodium alginate with poly(2-aminoethyl methacrylate hydrochloride). Furthermore, the films of the hybrid materials could be formed by means of the polymerization of the methacrylate monomer in the presence of sodium alginate, followed by the evaporation of the solvent.

Keywords: Alginate; hybrid material; Polysaccharide; Polymerization

1. Introduction

Novel procedures to prepare hybrid materials on the intimate mixture of natural or synthetic polymers have been extensively investigated (Crescenzi et al., 1997), for example, grafting of synthetic polymer chains onto polysaccharides such as dextran, starch, and chitin (Hoffmann, Kästner, Dönges, & Ehrler, 1996; Kobayashi, Tsuchida, Usui, & Akaike, 1997; Van Dijk-Wolthuis, Kettenen-Vanden Bosch, Van der Kerk-van Hoof, & Hennink, 1977). Chitosan, a natural aminopolysaccharide, has been used as the typical polymeric template for preparation of grafting and complexation, as well as interpenetrating polymeric network (IPN) materials, with synthetic polymers (Cerrai et al., 1996; Chavasit, Kienzle-Sterzer, & Torres, 1988; Kim et al., 2002; Lee, Kim, & Lee, 2000; Prashanth & Tharanathan, 2003; Wang, Li, Lu, & Wang, 1997; Wang, Li, Lu, Wang, & Zhong, 1996). For example, ionic complexes are formed by the interaction of the carboxylic groups of acrylic acids with the amino groups in chitosan, which can be converted into a highly swollen hybrid material by radical polymerization of acrylic acids in the complexes (Peniche et al., 1999).

On the other hand, alginic acid is a well-known natural polysaccharide, which is consisting of (1→4) linked β-D-mannuronic acid and α-L-guluronic acid residues of widely varying composition and sequence as shown in Fig. 1. Alginic acids are quite abundant in nature since they occur both as a structural component in marine brown algae (*Phaeophyceae*), comprising up to 40% of the dry matter, and as capsular saccharides in soil bacteria. Due to the presence of the carboxylic acid groups in the saccharide residues, alginic acid has an anionic nature, forming alginate salts with cationic metals, such as Ca^{2+} and Na^{+}. Calcium alginate is insoluble and appears the swelling behavior in water, whereas sodium alginate is soluble in water. Therefore, sodium alginate has been inspired to use as an anionic template for

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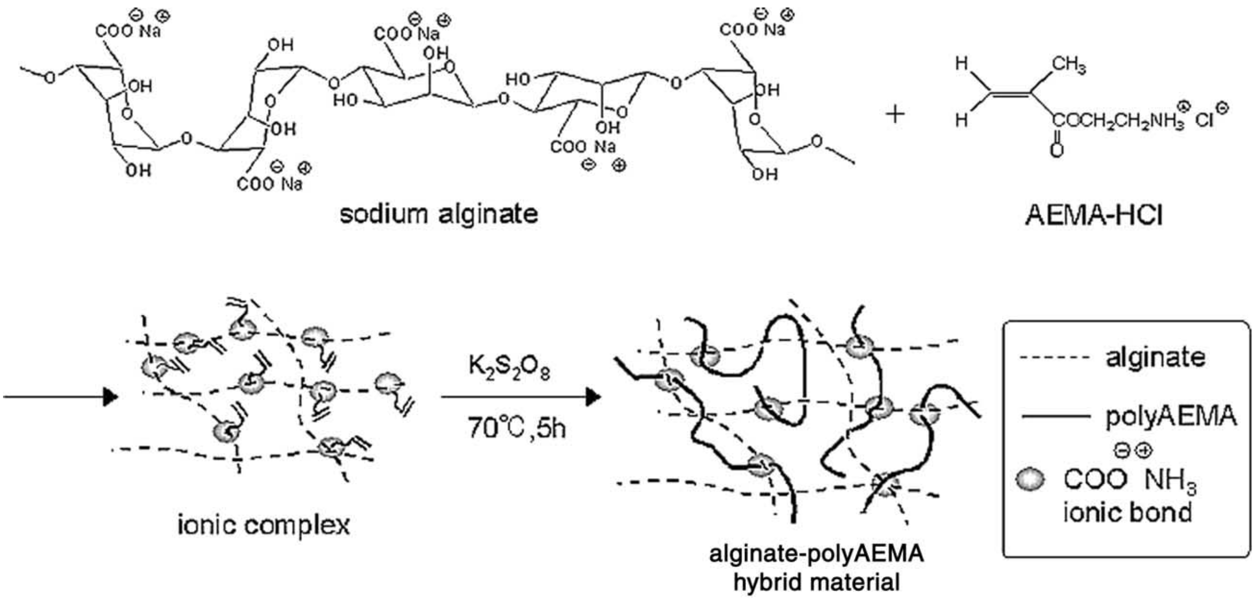


Fig. 1. Schematic image for preparation of hybrid material by polymerization of 2-aminoethyl methacrylate hydrochloride in the presence of sodium alginate.

formation of the hybrid materials combining with cationic polymers by means of the polymerization as the case of chitosan described above. The (semi-)IPN materials from alginate and synthetic polymers have been prepared, e.g. semi-IPN hydrogels composed of sodium alginate and poly(*N*-isopropylacrylamide) (Ju, Kim, Kim, & Lee, 2002). To our best knowledge, however, preparation of the hybrid materials using sodium alginate combining with cationic monomers, followed by polymerization has scarcely been studied. Recently, synthesis of alginate/poly(diallyldimethylammonium chloride) IPN hydrogels was reported, which might be based on this methodology (Kim, Yoon, & Kim, 2004; Kim, Yoon, Lee, Lee, & Kim, 2003). In this paper, we describe preparation of a new alginate-polymethacrylate hybrid material by radical polymerization of a cationic methacrylate monomer in the presence of sodium alginate. The image for procedures forming such the material is shown in Fig. 1. As the cationic monomer, 2-aminoethyl methacrylate hydrochloride (AEMA-HCl) was employed.

2. Experimental

2.1. Materials

Sodium alginate (degree of polymerization = ca. 450) was purchased from NACALAI TESQUE, Inc., Kyoto, Japan. Other reagents were used as received. Poly(AEMA-HCl) was prepared by radical polymerization of AEMA-HCl initiated with potassium persulfate in water at 70 °C. The product polymer was purified by precipitation into acetone.

2.2. Preparation of alginate-polymethacrylate hybrid material

To a viscous solution of sodium alginate (0.50 g) in water (25 mL) was added AEMA-HCl ($NH_3^+/COO^- = 0.25-1.0$), and the mixture was stirred for 6 h at room temperature. Potassium persulfate (0.05 equivalents for AEMA-HCl) was added to the mixture and the solution was heated at 70 °C for 5 h. After the reaction mixture was cooled to room temperature, a precipitated product was isolated by centrifugation, washed three times with water, and dried under reduced pressure to give the hybrid material.

2.3. Preparation of a mixture of alginate with polymethacrylate

Poly(AEMA-HCl) ($NH_3^+/COO^- = 1.0$) was added to an aqueous solution of sodium alginate (1.0 wt%), and the mixture was stirred overnight at room temperature. The obtained solution was dialyzed using cellulose tube, followed by concentration. The product was dried under reduced pressure to give the mixture of alginate with polyAEMA.

2.4. Preparation of alginate-polymethacrylate hybrid film

AEMA-HCl ($NH_3^+/COO^- = 0.25-1.0$) was added to a viscous solution of sodium alginate (0.50 g) in water (25 mL), and the mixture was stirred for 6 h at room temperature. Potassium persulfate (0.05 equivalents for AEMA-HCl) was added to the mixture and the solution was heated at 70 °C. When the mixture became turbid, it was

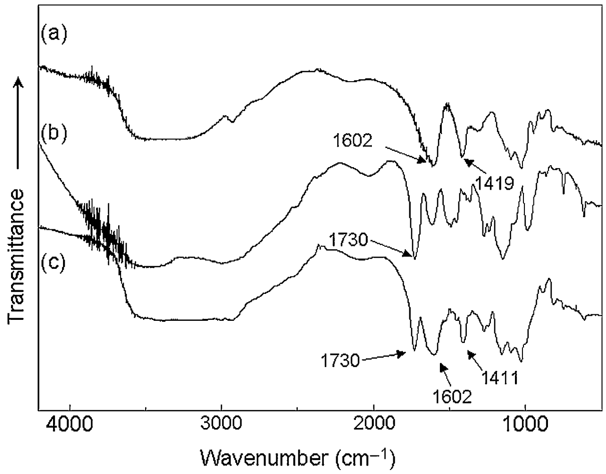


Fig. 2. IR spectra of sodium alginate (a), poly(AEMA-HCl) (b), and product (c).

cooled to room temperature and additionally stirred for 1 h at that temperature. The suspension was transferred to petri-dish (diameter 70 mm) and heated at 80 °C in oven to give a hybrid film.

2.5. Measurements

Elemental analyses were performed by Yanagimoto CHN corder MT-6. NMR spectra were recorded on Bruker DPX400 and ORX500 spectrometers. IR spectra were recorded on a Shimadzu FTIR-8300 spectrometer. TG analyses were performed on a Seiko TG/DTA 220 thermal analyzer at a heating rate of 10 °C/min. DSC measurements were carried out using a heating rate of 10 °C/min from room temperature to 300 °C on a Shimadzu DSC-60. Before analyses, the sample was preheated to 150 °C, kept at that temperature for 5 min, and then cooled to room temperature.

3. Results and discussion

3.1. Preparation of alginate-polymethacrylate hybrid material

Attempt for formation of alginate-polymethacrylate hybrid material was made by radical polymerization of AEMA-HCl in the presence of sodium alginate in water as follows (Fig. 1). First, an aqueous solution of sodium alginate was prepared and $0.25-1.0$ equivalents of AEMA-HCl monomers toward carboxylates in alginates were added. Subsequently, ion exchanges may be occur to give AEMA salts of alginates. Then, the radical polymerization was carried out by potassium persulfate as a water-soluble initiator at 70 °C. The solution gradually became turbid to precipitate the product.

The isolated product was insoluble in any organic solvents and water. Fig. 2 shows the IR spectra of sodium alginate, poly(AEMA-HCl), and the product. The IR spectrum of the product (Fig. 2(c)) exhibited the characteristic absorptions due to both alginate and polyAEMA. The absorptions at 1602 and 1411 cm^{-1} were assigned to the asymmetric and symmetric stretching of COO$^-$ groups in alginate, respectively (Kim et al., 2004), while the absorption at 1730 cm^{-1} was ascribed to C=O of polyAEMA (Ling, Brahmachary, Xu, Svec, & Frechet, 2003). These IR data supported that the product was composed of alginate and polyAEMA. However, the IR spectrum of the mixture of sodium alginate with poly(AEMA-HCl) (preparation procedures are described in the next paragraph) exhibited the similar patterns to those of Fig. 2(c). Therefore, the remarkable difference between the product and the mixture was not found from the results of the above IR analysis.

Table 1 shows the elemental analysis data of the products obtained by the feed ratios of NH$_3^+$ to COO$^-$ ranging $0.25-1.0$. No existence of Cl element in all products was observed by the analyses, indicating occurrence of complete ion exchanges between –COONa and –NH$_3$Cl. These data were compared with those of the mixture of alginate with poly(AEMA-HCl). The mixture was prepared by mixing sodium alginate and independently prepared poly(AEMA-HCl) (NH$_3^+$/COO$^-$ = 1.0) in water, followed by concentration of the solution after the dealysis, which was insoluble in any solvents. The elemental analysis result of the mixture exhibited to exist 2.5 wt% of Cl element. From the value, it was calculated that ca. 22% of the amino groups of polyAEMA in the mixture were still left as the hydrochloride forms accompanied with the equimolar amount of COONa groups in the alginate. This can be explained by the incomplete ion exchange in the mixture, indicating that

Table 1
Yields, elemental analysis data, and NH$_3^+$/COO$^-$ ratios of products in comparison with data of a mixture

Sample	Yield (%)[a]	Elemental analysis (%)				NH$_3^+$/COO$^-$	
		C	H	N	Cl	Feed ratio	Product[b]
Product-0.25	18.3	38.76	6.52	3.10	0	0.25	0.70
Product-0.50	51.8	40.83	6.75	3.57	0	0.50	0.82
Product-0.75	87.1	42.95	6.58	3.85	0	0.75	0.86
Product-1.0	90.9	41.53	6.83	3.94	0	1.0	0.95
Mixture-1.0	–	39.21	6.30	3.75	2.54	1.0	–

[a] Insoluble parts from the reaction mixtures.
[b] NH$_3^+$/COO$^-$ ratios in the products were calculated by elemental analysis data.

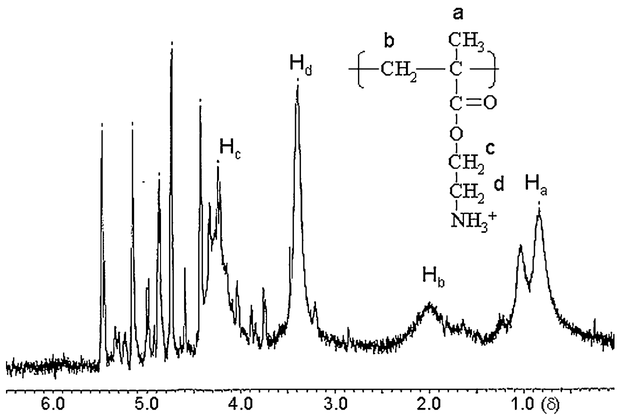


Fig. 3. ^{1}H NMR spectrum of hydrolysis mixture of product ($NH_3^+/COO^- =$ 0.95) in H_2SO_4–D_2O.

the alginate-polymethacrylate hybrid materials having the perfect –$COONH_3^-$ groups were available only by the polymerization of the cationic methacrylate monomer in the presence of alginate.

From the elemental analysis data, the molar ratios of NH_3^+ to COO^- in the products obtained by the polymerization method were calculated (Table 1). When the feed ratio of NH_3^+ to COO^- was 1.0, the NH_3^+/COO^- ratio in the product (0.95) was relatively close to the feed. According to decreasing the feed ratios of NH_3^+ toward COO^-, however, the ratios of NH_3^+ groups in the products increased than the feed ratios. The yields of the products precipitated from the reaction mixtures decreased with decreasing the feed ratios of NH_3^+ toward COO^-. These observations indicated that the products became insoluble in the reaction solutions when the relative high molar ratios of the carboxylate groups in alginate formed the ionic salts with polyAEMA. In the case of the lower NH_3^+ feed ratios, therefore, the fractions with the higher ratios of NH_3^+ than the feed ratios were precipitated rapidly and the rest of the fractions with the lower ratios of NH_3^+ was soluble to stay in the reaction solutions. Accordingly, the yields of the precipitated fractions were relatively low.

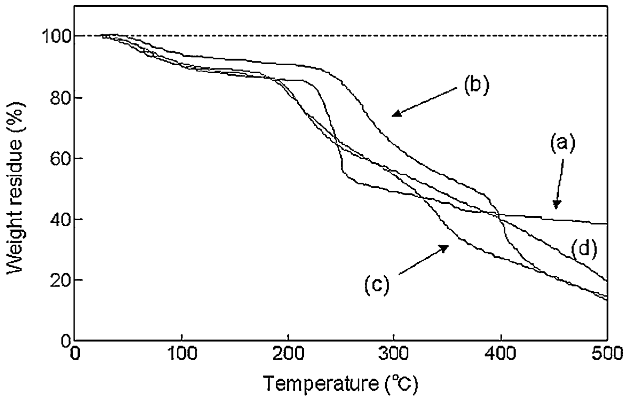


Fig. 4. TG curves of sodium alginate (a), poly(AEMA-HCl) (b), product ($NH_3^+/COO^- = 0.95$) (c), and mixture (d).

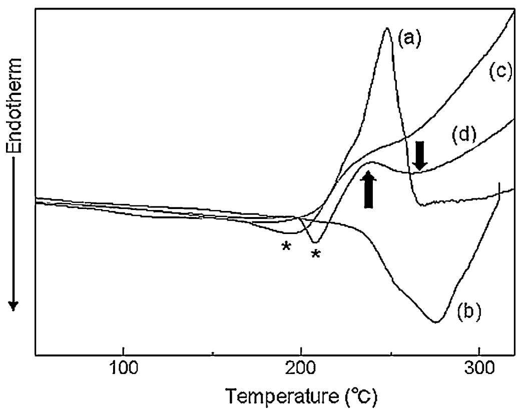


Fig. 5. DSC traces of sodium alginate (a), poly(AEMA-HCl) (b), product ($NH_3^+/COO^- = 0.95$) (c), and mixture (d).

To confirm that the products were actually consisting of polyAEMA, acid hydrolysis of the product ($NH_3^+/COO^- =$ 0.95) was carried out in 70% sulfuric acid–D_2O solution. When the product was kept in the acid solution at room temperature, the mixture gradually became homogeneous, attributed to occurrence of the glycosidic bond cleavage in the polysaccharide chains under such strong acidic conditions. The hydrolyzed products were directly analyzed by ^{1}H NMR measurement. As shown in Fig. 3, the signals H_a–H_d assigned to polyAEMA were observed in the ^{1}H NMR spectrum of the products. These NMR peaks' patterns were similar to those of the polymers of the amino-functionalized methacrylates reported in the previous study (Geurts et al., 1999). The hydrolysis experiment supported that the radical polymerization of AEMA took place in the presence of alginate to give the insoluble products consisting of polyAEMA.

3.2. Thermal analyses of the product

TG analyses of the product ($NH_3^+/COO^- = 0.95$), a mixed material (mixture), sodium alginate, and poly

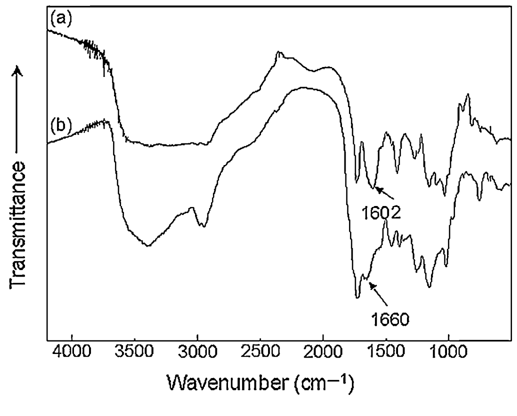


Fig. 6. IR spectra of product ($NH_3^+/COO^- = 0.95$) (a) and after heating at 200 °C for 30 min (b).

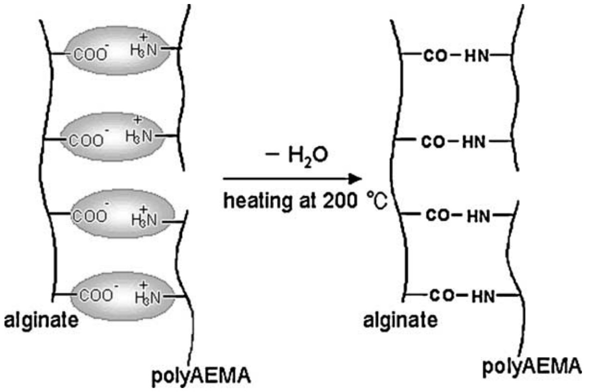
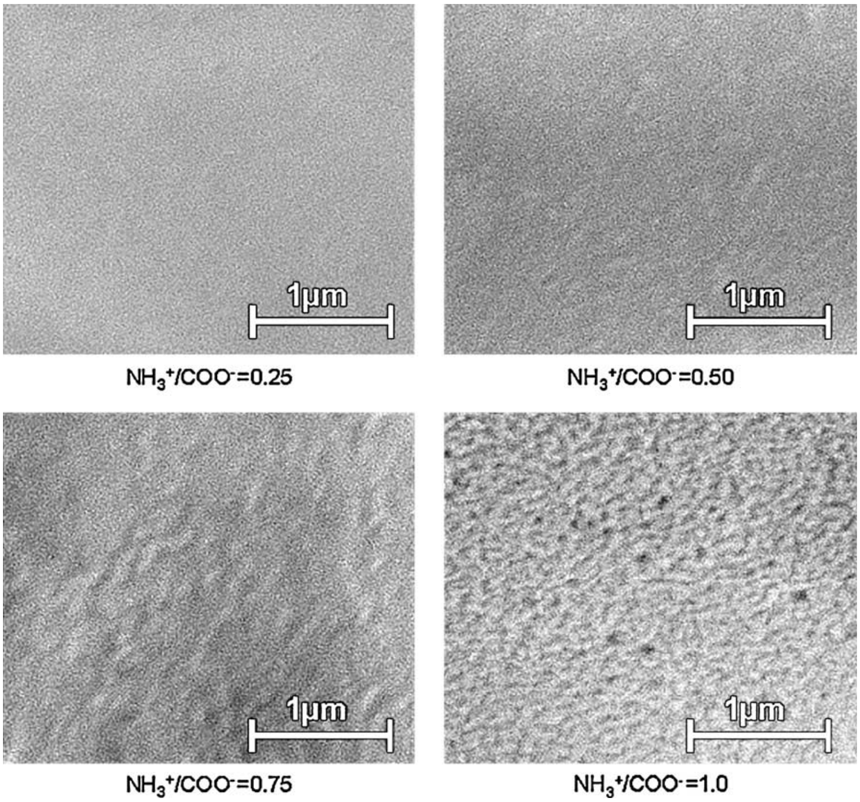


Fig. 7. Schematic image of dehydrative amidation between carboxylate and ammonium groups in product.

(AEMA-HCl) were performed (Fig. 4). The TG curves of the product and the mixture ((c) and (d), respectively) exhibited similar weight loss patterns at the temperatures below 280 °C. At higher temperatures, different profiles were obtained, in which the product gave more frequent weight losses than those of the mixture.

Fig. 5(c) shows the DSC trace of the product (NH_3^+/COO^- = 0.95) in comparison with that of sodium alginate (a), poly(AEMA-HCl) (b), and the mixture (d). The DSC traces of sodium alginate and poly(AEMA-HCl) exhibited an exothermic and endothermic peaks at 247 and 273 °C, respectively. The two peaks also appeared in the DSC trace of the mixture (indicated by arrows), whereas obvious peaks at around those temperatures were not observed in the DSC trace of the product. These DSC results indicated that the product was the network structure composed of alginate and polyAEMA, whereas the phase separation of these two polymers may be partly present in the mixture. The difference of the TG curves between the product and the mixture may also be caused by this reason. Furthermore, characteristic endothermic peaks at 197 and 208 °C were observed in the DSC traces of the product and the mixture, respectively (indicated by asterisks), which did not appear in the DSC traces of sodium alginate and poly(AEMA-HCl). In addition, the weight losses took place at around these temperatures as shown in the TG curves of the product and the mixture (Fig. 4(c) and (d)). From these data, it can be assumed that some endothermic reaction of the alginate with polyAEMA occured in both the product and the mixture at these temperatures. To confirm the reaction further, the IR analysis was performed after the product was heated at 200 °C for 30 min. The IR spectra before and after heating the product are shown in Fig. 6(a) and (b), respectively. The IR spectrum in Fig. 6(b) showed disappearance of the carbonyl absorption at 1602 cm^{-1} due to the carboxylate and appearance of the new carbonyl absorption at 1660 cm^{-1} due to the amide. In the previous study, the carbonyl absorption of the amidated alginate was



$NH_3^+/COO^-=0.25$ $NH_3^+/COO^-=0.50$

$NH_3^+/COO^-=0.75$ $NH_3^+/COO^-=1.0$

Fig. 8. SEM pictures of hybrid films obtained by various feed ratios; $NH_3^+/COO^- = 0.25 - 1.0$.

also observed at that area (Magnani, Rappuoli, Lamponi, & Barbucci, 2000). These results indicated occurrence of the dehydrative amidation between the carboxylate and ammonium groups in the product, giving the new material linked to the amide groups as shown in Fig. 7.

3.3. Film formation of the product

Film formation of the alginate-polyAEMA hybrid material was investigated as follows. The polymerization of AEMA-HCl in the presence of sodium alginate was carried out by the procedures similar to those described above. When the mixture became turbid, it was cooled to room temperature to stop the polymerization. The obtained suspension was transferred to petri-dish and heated at 80 °C in oven to evaporate the solvent, forming a film. Surface morphologies of the films of varying NH_3^+/COO^- feed ratios were confirmed by SEM analyses. As appeared in Fig. 8(a), the film obtained by the NH_3^+/COO^- feed ratio = 0.25 had a relative flat surface. The surface morphologies became rougher with increasing the feed ratios of NH_3^+, probably due to favorable formation of network structures.

4. Conclusion

We have prepared the alginate-polymethacrylate hybrid material by means of the radical polymerization of 2-aminoethyl methacrylate hydrochloride in the presence of sodium alginate in water. The product was gradually precipitated with progress of the polymerization. The IR and elemental analyses supported that the product was composed of the alginate and polymethacrylate. The data of the thermal analyses of the product were different from those of the mixture of sodium alginate and polymethacrylate. Furthermore, the film formation of the products was achieved and the surface morphologies were confirmed by the SEM analyses.

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