

Preparation and Characterization of Water-Soluble Polyacrylate Sodium Modified by Organomontmorillonite

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ABSTRACT: Water-soluble high intrinsic viscosity organomontmorillonite modified polyacrylate sodium (OMMT-modified PNaA) was prepared via an *in situ* intercalation adiabatic polymerization of sodium acrylate in the presence of OMMT. The FTIR and XRD analyses correspond to the OMMT-modified PNaA with exfoliated structure of OMMT. The influences of prepared conditions on intrinsic viscosity and dissolving time of the modified polymers had been investigated in this study. It was found that the incorporation of as little as 0.1 wt % of OMMT added to PNaA matrix could be effective to enhance intrinsic viscos-

ity of the modified PNaA. TGA and DSC studies confirmed the enhancement of the thermal stability of the OMMT-modified PNaA when compared with PNaA. Furthermore, the solution behavior studies of the modified PNaA showed the "antipolyelectrolyte" effect and high "antishearing" property. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 915–920, 2008

Key words: sodium acrylate; organomontmorillonite; *in situ* intercalation adiabatic polymerization; water-soluble; characterization

INTRODUCTION

Pristine layered silicates usually contain hydrated Na⁺ and Ca²⁺ ions¹ and can interact with hydrophilic polymers, such as poly(ethylene glycol),² poly(acrylic acid),³ and amylopectin⁴ by blend method. To enhance the strength of interface between layered silicates and polymer matrix, one of recent interests prepared polymer/clay nanocomposites is used to *in situ* intercalation polymerization of monomer in the presence of organomontmorillonite (OMMT), which can make the normally hydrophilic silicate surface organophilic. In general, OMMT could be prepared by ion-exchange reaction of montmorillonite with cationic surfactants including quaternary alkylammonium and alkylphosphonium cations.^{5,6}

The incorporation of a small amount of organic clay to polymers will result in the outstanding improvement of general properties compared to neat polymers, for instance, gas permeability,⁷ better mechanical properties, and higher thermal stability.⁸ Yeh et al.¹ reported the polyacrylamide-clay nanocomposite materials prepared by an *in situ* UV

photopolymerization using acrylamide as an intercalation agent, the results of TGA and DSC studies confirmed the enhancement of the thermal stability of the polyacrylamide-intercalated materials. The O₂ and N₂ molecular permeability of the nanocomposite showed that the dispersion of clay platelets in polyacrylamide promoted the molecular barriers of the as-prepared membranes. Yu et al.⁹ prepared a series of poly(vinyl alcohol)-clay nanocomposite materials via an *in situ* free radical polymerization of vinyl acetate monomer and followed by direct-hydrolysis with NaOH solution. The incorporation of montmorillonite nanolayers in poly(vinyl alcohol) matrix arose from an increase in thermal decomposition temperature, char yield, glass transition temperature, and mechanical strength based on TGA, DSC, and DMA studies. Singhal et al.¹⁰ also synthesized nanocomposites of bentonite with poly(aniline-co-methacrylic acid) copolymer by *in situ* intercalative polymerization technique. The copolymeric nanocomposite showed the highest thermal stability than those of polyaniline and poly(methacrylic acid). Their swelling behavior suggests that these nanocomposites hold potential for utilization in absorption of toxic materials from waste water. However, relatively few studies have been conducted to prepare water-soluble organomontmorillonite-modified (OMMT-modified) polymers.^{4,11} In this article, we first prepared water-soluble high intrinsic viscosity

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TABLE I
Prepared Conditions and Properties of the OMMT-Modified PNaA^a

Sample code	NaA (g)	OMMT (g) (wt %)	APS + SBF (mg) (wt %)	AIBA (mg) (wt %)	pH	[η] (dL/g)	T_d (min)
H-1	50	0.125 (0.25)	3.45 (0.069)	4.15 (0.083)	6	12.9	60
H-2	50	0.125 (0.25)	3.45 (0.069)	4.15 (0.083)	8	16.2	40
H-3	50	0.125 (0.25)	3.45 (0.069)	4.15 (0.083)	10	18.9	29
H-4	50	0.125 (0.25)	3.45 (0.069)	4.15 (0.083)	11	19.1	28
S-1	50	0.125 (0.25)	2.20 (0.044)	8.35 (0.167)	10.8	14.8	24
S-2	50	0.125 (0.25)	3.45 (0.069)	8.35 (0.167)	10.8	14.1	23
S-3	50	0.125 (0.25)	4.40 (0.088)	8.35 (0.167)	10.8	13.2	22
S-4	50	0.125 (0.25)	6.00 (0.120)	8.35 (0.167)	10.8	11.8	17
A-1	50	0.125 (0.25)	3.45 (0.069)	3.35 (0.067)	10.8	19.6	36
A-2	50	0.125 (0.25)	3.45 (0.069)	4.15 (0.083)	10.8	19.2	29
A-3	50	0.125 (0.25)	3.45 (0.069)	6.25 (0.125)	10.8	16.1	26
A-4	50	0.125 (0.25)	3.45 (0.069)	8.35 (0.167)	10.8	14.8	23
T-0	50	–	3.45 (0.069)	4.15 (0.083)	10.8	15.4	19
T-1	50	0.050 (0.10)	3.45 (0.069)	4.15 (0.083)	10.8	18.2	25
T-2	50	0.250 (0.50)	3.45 (0.069)	4.15 (0.083)	10.8	18.9	30
T-3	50	0.325 (0.75)	3.45 (0.069)	4.15 (0.083)	10.8	18.3	35
T-4	50	0.500 (1.00)	3.45 (0.069)	4.15 (0.083)	10.8	17.8	45
T-5	50	0.625 (1.25)	3.45 (0.069)	4.15 (0.083)	10.8	16.3	60
T-6	50	0.750 (1.50)	3.45 (0.069)	4.15 (0.083)	10.8	16.0	80

^a NaA weight was based on the weight of 100% neutralized acrylic acid; APS : SBF weight ratio = 1.3 : 1.0.

OMMT-modified polyacrylate sodium (PNaA) using an *in situ* intercalation adiabatic polymerization of sodium acrylate with OMMT in aqueous solution. The influences of prepared conditions on intrinsic viscosity and dissolving time of modified polymers had been investigated in this study. FTIR, XRD, TGA, DSC, and solution behavior analyses revealed the intercalated structure and properties of the modified polymers.

EXPERIMENTAL

Materials

Acrylic acid (Tianjin Chemical Reagent, Tianjin, China) was purified from active carbon, prior to use, the desired pH value of sodium acrylate (NaA) solution was obtained via acrylic acid neutralized with 5.0 mol/L NaOH solution. Hexadecyl-trimethylammonium bromide (HDTMAB, Tianjin Chemical Reagent Manufacturer, Tianjin, China) was used without further purification. Sodium montmorillonite (MMT) powder with a cation-exchange capacity of 100 mequiv./100 g was supplied by Fenghong Clay Chemical (Huzhou, China). Organomontmorillonite (OMMT) was prepared according to literature.¹² Briefly, MMT (10 g) placed in a 500-mL flask was suspended in 200 mL distilled water and stirred for 2 h. After the suspensoid was heated to 70°C, the HDTMAB (6.67 g) was added into the flask with vigorous stirring for 6 h. Then the precipitate was filtered and washed several times with distilled water to remove all bromide ions.¹² Finally, the acquired gray-white OMMT was dried in a vacuum oven at

70°C for 48 h. Ammonium persulfate (APS, Guangzhou Chemical Manufacturer, Guangzhou, China) and sodium bisulfoxylate formaldehyde (SBF, Shanghai Runjie Chemical Reagent, Shanghai, China) and 2,2'-azobis(2-amidinopropen)-dihydrochloride (AIBA, Shanghai Hengyi Chemical, Shanghai, China) were used as supplied. Water was doubly distilled. Other reagents were GR grade and were used as received.

Preparation of OMMT-modified PNaA via *in situ* intercalation adiabatic polymerization

A sodium acrylate solution (~ 35 wt %) containing 50 g of NaA (see Table I) was placed into a well-stirred suspensoid of OMMT in a 200-mL flask provided with a magnetic stirrer. Then an aqueous solution of AIBA (20 mmol/L) was added to the mixture. The system was purged with N₂ for 15 min. The flask was sealed with a rubber septum and insulated, and took place at room temperature. Subsequently, the aqueous solutions of APS (10 mmol/L) and SBF (10 mmol/L) were introduced into the reaction system under stirring, using syringes, respectively. A thermometer that penetrated the rubber septum to the center of the concentrated solution was employed to measure the temperature. As soon as the *in situ* intercalation adiabatic polymerization system became viscous solution, the stirring could no longer be continued. Whenever the system attained a maximum temperature, external heating in a water bath was provided for maturation of keeping temperature. After the polymerization was conducted for 4 h, the gelatinous product was taken

out from the flask, cut-up, and dried in a vacuum oven at 50°C for 24 h. Weight ratio of the product to the total feed before the *in situ* intercalation adiabatic polymerization was taken as the yield of OMMT-modified PNaA, which was greater than 95 wt %. In addition, the PNaA was also synthesized in our lab with the same method but no added OMMT.

Characterization of the products

X-ray diffraction (XRD) was carried out on powder samples to evaluate the degree of PNaA intercalation between the clay layers, using a Japan Rigaku D/MAX-III X-ray diffractometer (Rigaku, Tokyo, Japan) with Cu K α radiation operated at 30 KV and 40 mA. The samples were scanned in 2 θ range from 1 to 10, at the rate of 5°/min.

Fourier transform infrared (FTIR) spectra of the products (KBr pellet) were recorded with a Nicolet 760 MAGNA-IR FTIR spectrometer (Nicolet, WI, USA). Thermogravimetric analysis (TGA) of the products were contained in flowing N₂ on a Germany TG209 thermogravimeter (Netzsch, Selb, Germany) with a temperature increasing rate of 10°C/min. Melting behavior of the materials was examined by a TA MDSC2910 differential scanning calorimetry (DSC, TA, New Castle, USA) under a N₂ atmosphere at a heating rate of 20°C/min.

The intrinsic viscosity ($[\eta]$, dL/g) of the OMMT-modified PNaA was measured as our earlier paper.¹³ The reduced viscosity (η_{red} , mL/g) measurements were carried out with a sample concentration of 1 wt %. The dissolving time (T_d , min) of the materials was measured via slowly adding 0.1 g of product powder to 200 g distilled water, stirring with the rate of 200 rpm in water bath at 45°C.

RESULTS AND DISCUSSION

Preparation of OMMT-modified PNaA

The OMMT-modified PNaA was prepared by *in situ* intercalation adiabatic polymerization with various amounts of OMMT. To obtain water-soluble high intrinsic viscosity OMMT-modified PNaA, polymerization conditions, such as solution pH value, redox initiator, and promoter concentration, and OMMT content must be optimized. Table I shows the influences of polymerization conditions on the intrinsic viscosity and dissolving time of the OMMT-modified PNaA.

The effect of the original solution pH value on intrinsic viscosity and dissolving time of the OMMT-modified PNaA can be seen in Table I (H-series). The intrinsic viscosity increased with increasing pH, and then tending to a nearly steady value (~ 19 dL/g). Furthermore, the dissolving time was shortened with increasing the pH. After pH ≥ 10 , the dissolv-

ing time was shortened to ~ 30 min. This is because strong basic solution could avoid the formation of crosslinking polymer.¹⁴ However, the aggregation extent of PNaA chains could increase in solution of high pH (pH > 12).¹⁵ The experimental result showed that it was available for controlling the pH 10.8 in the original solution.

The effects of the redox initiator (total concentration of APS and SBF, APS : SBF weight ratio = 1.3 : 1.0) and AIBA promoter concentrations on intrinsic viscosity and dissolving time of the OMMT-modified PNaA can be shown in Table I S-series and A-series, respectively. In theory, the length of the polymeric dynamic chain (ν) is the inverse ratio with square root of initiator concentration (I), that is, $\nu \propto I^{-1/2}$. So the results of decreasing the redox initiator and/or AIBA promoter concentration can increase the intrinsic viscosity of the products. However, when the initiator and/or promoter concentration was further decreased the residual monomer concentration might increase. This could cause the polymeric crosslinking during drying gelatinoid and powder could have poor aqueous solubility. In addition, there was a small amount of transition metal ions in OMMT, such as Fe³⁺ and Cu²⁺, etc., so the initiator could also be partially consumed.¹⁶ Moreover, the effect of AIBA concentration on intrinsic viscosity and dissolving time of the OMMT-modified PNaA is more notable than that of redox initiator (see Table I), because the carbon radical generated by decomposition of AIBA is absent from dehydrogenation power, which is beneficial for the preparation of water-soluble high intrinsic viscosity modified products.¹⁷ The optimum redox initiator and AIBA concentrations were sure to be 0.069 and 0.083 wt % (compared to monomer), respectively.

Table I (T-series and A-2) also presents the effect of the OMMT content in the feed on the intrinsic viscosity and dissolving time of the OMMT-modified PNaA. It can be seen that the intrinsic viscosity of the modified PNaA could be enhanced than that of PNaA with adding to OMMT, but when the OMMT content was higher than 0.25 wt % (compared to monomer), the intrinsic viscosity slowly decreased with an increase in the OMMT content. This was because of two effects: when *in situ* polymerization of the intercalated monomers proceeded, polymeric chains or segments stay in the vicinity of the clay surface, which could lead to the formation of micro-crosslinked polymer system containing OMMT core. It was natural that the intrinsic viscosity was enhanced. Moreover, after the polymerization of sodium acrylate, exfoliated OMMT nanolayers were well dispersed in the polymer matrix, providing a strong absorbability to the carboxylate groups of polymer chains. Inter- or intramolecular-ionic bonding occurs between anionic PNaA and cationic

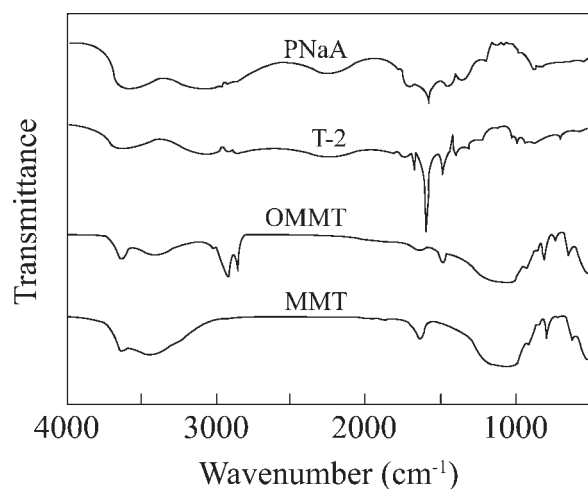


Figure 1 FTIR spectra of MMT, OMMT, PNaA, and OMMT-modified PNaA (sample T-2, Table I).

OMMT nanolayers, which could also raise the systematic intrinsic viscosity. However, when an excessive amount of the OMMT was added the polymer molecular chains could aggregate with increasing the crosslinking level and physical absorption. This resulted in the decrease of the intrinsic viscosity. The dissolving time of T-series and A-2 samples can be seen in Table I, the greater the content of OMMT, the longer the dissolving time, but it remained longer than that of PNaA. This was due to formation of more crosslinking points between polymer chains and the clay layers with increasing the content of OMMT.

Investigation on the structure

The representative FTIR spectra of the MMT, OMMT, PNaA, and OMMT-modified PNaA (sample T-2; Table I) are shown in Figure 1. The characteristic vibration bands of PNaA are at 1561 cm^{-1} ($-\text{COONa}$) and 1409 cm^{-1} ($-\text{COOH}$), and those of MMT and OMMT are shown at 1040 cm^{-1} ($\text{Si}-\text{O}$), 520 cm^{-1} ($\text{Si}-\text{O}-\text{Al}$), and 3625 cm^{-1} (lattice water $\text{O}-\text{H}$). The absorbances at 2920 and 2851 cm^{-1} ($\text{C}-\text{H}$) and 1472 cm^{-1} ($\text{C}-\text{N}$) can be seen in OMMT spectrum, which suggest that a cation-exchange reaction of interlayer Na^+ with alkylammonium ions had made the silicate hydrophilic layer organophilic. The presence of 3625 cm^{-1} broadening peak of $\text{O}-\text{H}$ and 1040 cm^{-1} peak of $\text{Si}-\text{O}$ characteristic vibration did not reveal any shift in Figure 1 spectrum of the OMMT-modified PNaA, compared to OMMT spectrum, which suggest the exfoliation of the OMMT clay in PNaA matrix.¹⁰

Figure 2 shows the XRD patterns of MMT, OMMT, and OMMT-modified PNaA (sample T-2; Table I). The XRD pattern of MMT contains a peak

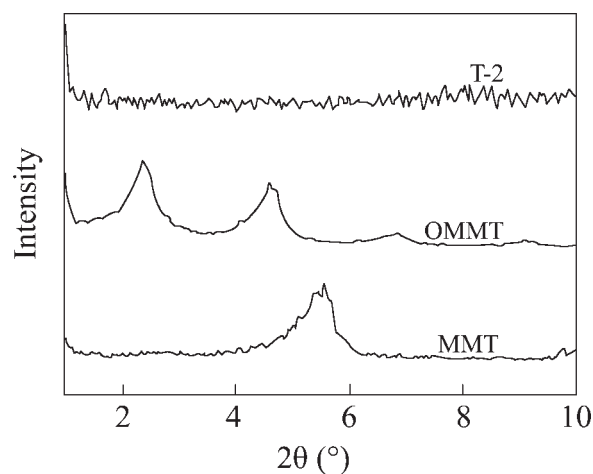


Figure 2 XRD patterns of MMT, OMMT, and OMMT-modified PNaA (sample T-2, Table I).

at $2\theta = 5.75^\circ$, corresponding to a basal spacing of 1.1 nm. The XRD peaks of OMMT show a better regularity from 1st to 3rd diffraction peaks, which possess an average d_{001} spacing of 3.8 nm. These results imply that the OMMT prepared via organic cation-exchange reaction not only effectively enlarged the lamellar spacing of MMT, but also formed a uniformly dispersive structure in MMT. For the OMMT-modified PNaA, there is a lack of any diffraction peak in $2\theta = 1-10^\circ$, indicating the possibility of having exfoliated silicate nanolayers of OMMT dispersed in a PNaA matrix.⁵ The result was beneficial for obtaining the water-soluble high intrinsic viscosity OMMT-modified PNaA, because this could form a microcrosslinked OMMT core-based polymer system.

Thermal properties

Figure 3 presents typical TGA curves of OMMT-modified PNaA (sample T-2; Table I) and PNaA. In

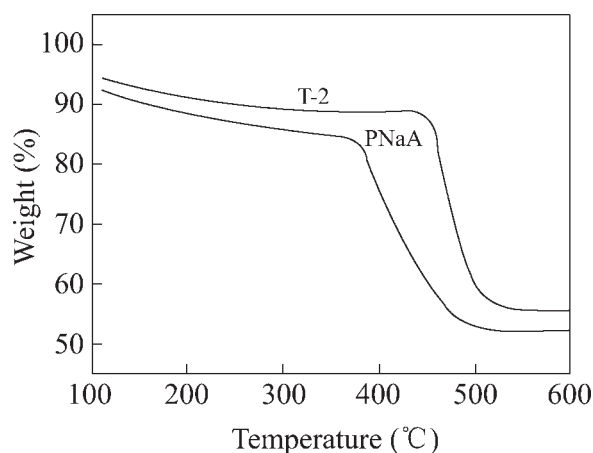


Figure 3 TGA curves of PNaA and OMMT-modified PNaA (sample T-2, Table I).

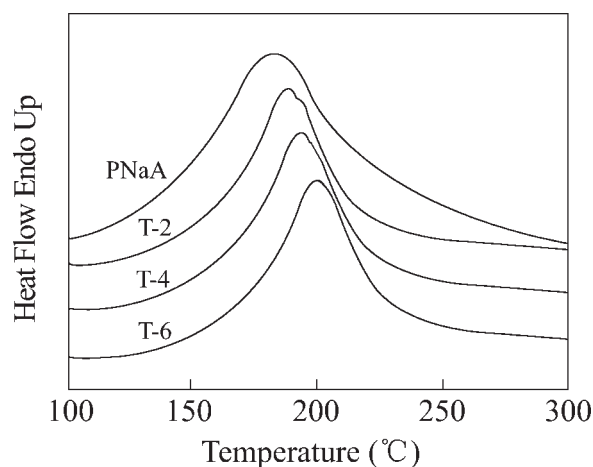


Figure 4 DSC thermograms of PNaA and a series of OMMT-modified PNaA (samples T-2, T-4, and T-6; Table I).

general, there appear to be a continuous weight loss until they reach the main structural decomposition of polymer during the investigated temperature range of 100–600°C. However, it should be noted that the fastest weight loss temperature stage shows the heat resistance of the products, the one of PNaA started at 370°C and ended at 500°C, and when 0.25 wt % of OMMT was added, the decomposition temperature of the modified PNaA raised at least 30°C. The improvement of the thermal properties was attributed to the high thermal stability of clays and their interactions with polymer matrix.¹⁸

The thermal properties could also be analyzed by DSC measurements, as illustrated in Figure 4, which shows the DSC results for a series of the OMMT-modified PNaA (samples T-2, T-4, and T-6; Table I) and PNaA. The PNaA exhibits an endotherm peak at 183.9°C, corresponding to the glass transition temperature (T_g) of PNaA. The incorporation of OMMT clay into PNaA caused an increase in T_g , which increased from 188.2, 193.8, to 200.2°C with the increasing OMMT contents of 0.50, 1.0, and 1.5 wt %, respectively. This is tentatively attributed to the confinement of interfacial adhesion between the layers and PNaA chains, and the confined extent might become stronger with an increasing concentration of OMMT in PNaA matrix.¹

Solution behavior

The effect of varying NaCl concentrations (0.0–1.0 mol/L) on reduced viscosity (η_{red}) of 1 wt % OMMT-modified PNaA (sample T-4, Table I) aqueous solution was investigated and compared to that of 1 wt % PNaA aqueous solution (see Fig. 5). Figure 5 shows that the reduced viscosity of the PNaA solution decreased with increasing NaCl concentration, obviously appearing as the “polyelectrolyte”

effect. However, for the OMMT-modified PNaA solution, at low NaCl concentrations (0.0, 0.1, 0.2, and 0.3 mol/L), the reduced viscosity increased linearly with increasing salt concentrations, suggesting an increase in aggregate size of polymer chains. At intermediate and high salt concentrations (0.4–1.0 mol/L), the reduced viscosity leveled off, indicating that the aggregate size became nearly constant. The increase in aggregate size could be viewed as an expansion of the PNaA molecular size when a higher salt concentration was present. The phenomenon was referred to as the “antipolyelectrolyte” effect.¹⁹ This could be attributed to the characteristic of *in situ* intercalation polymerization of water-soluble monomer in the presence of OMMT.¹¹ Because OMMT have strong absorption capacity towards the carboxylate groups, PNaA chains can aggregate on the exfoliated silicate nanolayers of OMMT. The salt can screen the electrostatic exclusion between the adjacent negatively charged carboxylate units on PNaA chains, thus promoting the PNaA chains absorption on the clay, which caused the polymeric molecular size as well as hydrodynamic volume to become large. So the intrinsic viscosity of the OMMT-modified PNaA solution continuously increased with increasing salt concentration.

Figure 6 presents changes in reduced viscosity of 1 wt % OMMT-modified PNaA (sample T-4, Table I) and PNaA aqueous solutions at a stirring rate of 300 rpm, as a function of stirring time. As was expected, for the PNaA solution, reduced viscosity showed a rapid decrease at shorter stirring times and then a slower reduction during longer stirring times. For the OMMT-modified PNaA, an interesting difference is that the η_{red} only was a slow reduction with stirring process. This was because the OMMT-modified PNaA held a microcrosslinked polymer system containing OMMT core, the influence of

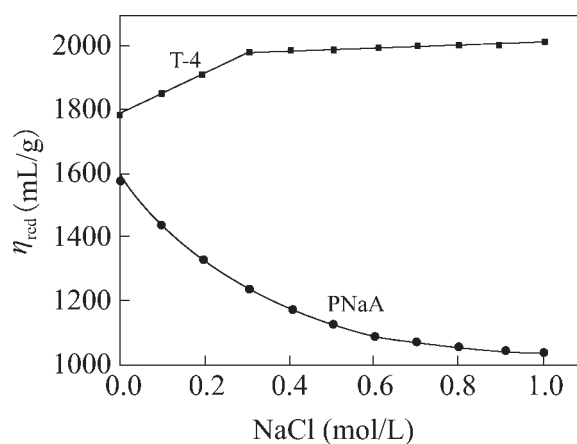


Figure 5 Effect of NaCl concentration on reduced viscosity (η_{red}) of 1 wt % OMMT-modified PNaA (sample T-4, Table I) and PNaA aqueous solutions.

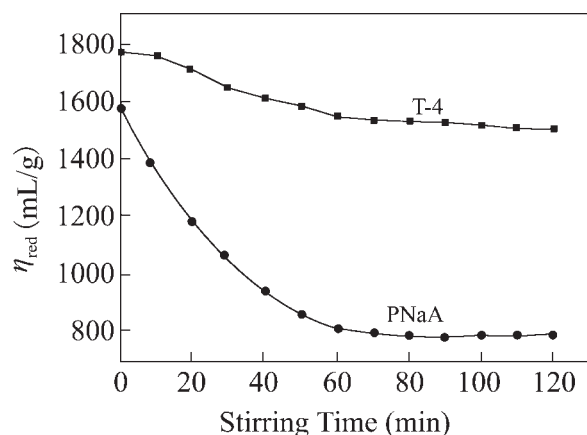


Figure 6 Effect of stirring time on reduced viscosity (η_{red}) of 1 wt % OMMT-modified PNaA (sample T-4, Table I) and PNaA aqueous solutions at stirring rate of 300 rpm.

breaking polymer chains on reduced viscosity was small than that of PNaA. In addition, thixotropy of OMMT induced from shearing also enhanced the “antishearing” property of the modified PNaA.²⁰

CONCLUSIONS

In this work, a series of the OMMT-modified PNaA materials were prepared by *in situ* intercalation adiabatic polymerization of sodium acrylate in the presence of OMMT. High intrinsic viscosity water-soluble OMMT-modified PNaA had been obtained by optimizing the reaction conditions. Exfoliated structure of the modified products was confirmed by FTIR and XRD analyses. Thermal decomposition temperature and T_g of the modified PNaA at low clay loading (e.g., 0.50 wt %) shifted towards the higher temperature range, compared to PNaA on the bases of TGA and DSC studies, which showed the improved thermal stability of the OMMT-modi-

fied PNaA. In addition, the reduced viscosity of the OMMT-modified PNaA in NaCl solution appeared on “antipolyelectrolyte” effect, and during continual stirring the low clay contents (e.g., 1.0 wt %) of the OMMT-modified PNaA still remained higher reduced viscosity than that of PNaA.

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