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Mechanical and Thermal Properties of Compression Molded Poly(acrylic acid) Salts with Multivalent Metal Ions

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Abstract : Films of zinc, calcium and aluminum salts of poly(acrylic acid) (PAA) were prepared from their powdery salts by compression molding at 190~200 °C, 600 MPa for 0.5 hr and their mechanical and thermal properties were investigated. From the results of the dynamic mechanical thermal analysis the storage modulus of each PAA salts exhibited about 20 GPa at room temperature because of highly intermolecular crosslinking of PAA by metal ions. Modulus of PAA calcium salt was 7 GPa even at 400 °C, while modulus of zinc salt and aluminum salt of PAA decreased abruptly above 200 °C. This decrease of modulus was attributed to the abrupt elimination of H₂O, which coordinated to metal ions, from specimens at high temperature.

1. Introduction

Recently, numerous high performance polymeric materials with high modulus and high strength have been used in industrial and space fields. A large number of studies on such materials have concerned with one-dimensional fiber forms. Whereas, there are few studies on three-dimensional high performance polymeric materials except composites like fiber reinforced plastics. Because the mechanical and thermal properties of unoriented isotropic polymers mainly depend on the weak interactions, such as van der Waals force and hydrogen bond, thus it is difficult for unoriented conventional polymers to be high performance materials.

Poly(acrylic acid) (PAA), a carboxylic acids polymer, is known to react with multivalent metal cations and forms highly crosslinked metal salts [1-3], which are insoluble in water and most of the organic solvents. For such polymers Coulomb force, the

strongest interaction, works between molecules and metal ions, hence it is considered to have an excellent potential as materials with high modulus, high strength and high heat resistance in the solid state. However, it is not easy for the PAA salts to be fabricated to shaped bodies owing to their high softening temperature, compared with conventional polymers. Therefore, little work has been made on such polymers except for the studies by Nielsen[4-6] and Konno[7-8], although those are attractive materials with excellent mechanical properties. Nielsen reported dynamic mechanical properties for only PAA zinc salts, and Konno investigated the modulus and strength of PAA metal salts at room temperature. It is necessary to investigate properties and structures of PAA metal salts in more detail.

In this study, we prepared PAA salts crosslinked by some multivalent metal ions (zinc (Zn²⁺), calcium (Ca²⁺), aluminum (Al³⁺)) and focused their mechanical, thermal properties and structures.

2. Experimental

2.1 Sample

2.1.1 Preparation of metal crosslinked PAA

PAA ($M_v = 150,000$) was purchased from Wako Pure Chemical Industries and was used without any purification. Multivalent metal chlorides, zinc chloride ($ZnCl_2$), calcium chloride ($CaCl_2$) and aluminum chloride ($AlCl_3$), were used as crosslinking agents of PAA. 7.20 g PAA was dissolved in 62.80 g deionized water with 4.00 g (100.0 mmol) sodium hydroxide, equivalent to carboxylic acids of PAA, and was neutralized to prepare sodium salts of PAA (PAA-Na). Next, 6.82 g (50.0 mmol) zinc chloride, and 5.55 g (50.0 mmol) calcium chloride and 4.44 g (33.3 mmol) aluminum chloride were dissolved in deionized waters, respectively. The aqueous solution of each metal chloride was poured into the neutralized PAA-Na solutions and then white precipitations of multivalent metal salts of PAA were developed because of intermolecular crosslinking of PAA by ion-exchange reaction between sodium ions and multivalent ions.

In this paper, PAA zinc salt, PAA calcium salt and PAA aluminum salt are represented by PAA-Zn, PAA-Ca and PAA-Al, respectively. Precipitations were washed by distilled water repeatedly to take away impurities. The cleaned PAA salts were, then, dried at 100°C under vacuum and were crushed into powder with a mortar.

2.1.2 Production of films

Films of PAA metal salts were produced by compression molding of powdery PAA salts at 190–200 °C, 600 MPa for 0.5 hr. These conditions were suitable to exclude air existing among powder. Each sample obtained was hard and glassy. PAA-Zn and PAA-Al were colorless and translucent, while PAA-Ca was white and opaque.

PAA homopolymer films were prepared by casting of the aqueous solutions to compare with PAA metal salts. PAA films were prepared by slowly drying at 40 °C and the films obtained had no defects.

All samples were preserved in a desiccator with diphosphorus pentoxide.

2.2 Measurements

Fourier transform infrared measurements (FT-IR) were performed by KBr method with a FT-IR

spectrometer (Perkin-Elmer1640). Measurement conditions were 64scans and resolution of 4cm^{-1} under a dry N_2 flow.

Inductively coupled plasma atomic emission spectroscopy (ICP-AES) was measured with SEIKO SRS 1500VR in order to determine the metal ion contents in PAA metal salts. Sample solutions for ICP-AES measurement were prepared by calcination of the salts at 600 °C for 2 hr and following dissolution in hydrochloric acid.

Wide-angle x-ray scattering (WAXS) experiments were performed on a RIGAKU Geigerflex 2028 diffractometer with $CuK\alpha$ radiation. The voltage and current of the x-ray source were 40 kV and 150 mA, respectively.

The storage modulus (E') was measured using a dynamic mechanical thermal analyzer (ITK Co., DVA-200) in a stretching mode with a frequency of 10 Hz and a heating rate of 6 °C/min. Specimens sized strip to $15\text{mm} \times 5\text{mm} \times 1\text{mm}$ were used.

Thermogravimetry-differential thermal analysis (TG-DTA) was carried out with a SEIKO TG-DTA at a heating rate of 20 K/min and sample weight of 10 mg under a N_2 flow.

The surface morphologies of the specimens were observed with a HITACHI S-2460 scanning electron microscope (SEM).

Gas chromatography-mass spectrometry (GC-MS) was performed with a JEOL JSM-DX303 GC-MS spectrometer.

3. Results and Discussion

3.1 Formation of PAA metal salts

Fig. 1 shows FT-IR spectra for PAA and its metal salts before molding. Carbonyl asymmetric stretching band [$\nu(C=O)$] of unneutralized $-COOH$ can be found at 1710cm^{-1} in the spectrum of PAA homopolymer. On the other hand, the PAA metal salts exhibited the shift of the $\nu(C=O)$ bands to lower wavenumbers around 1550cm^{-1} and the $\nu(C=O)$ of unneutralized $-COOH$ was weakened. This shift of $\nu(C=O)$ bands was caused by combining $-COO^-$ with metal cations[9]. Thus, precipitations were brought by intermolecular crosslinking of PAA chains with metal ions. Table 1 summarizes wavenumbers of $\nu(C=O)$ of PAA and its metal salts. $\nu(C=O)$ of unneutralized carboxylic acids

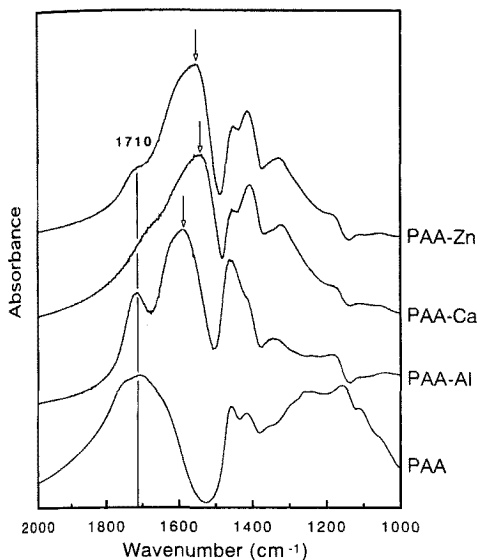


Fig. 1 FT-IR spectra for PAA and its metal salts. Arrows indicate the C=O stretching bands of -COO^- combined with multivalent metal ions.

at 1710 cm^{-1} , however, remains in each of the spectra for the metal salts.

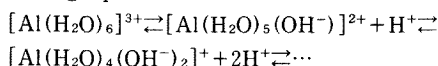
Table 1 Observed FT-IR wavenumbers of the peaks of $\nu(\text{C=O})$ for PAA and its metal salts.

Polymer	$\nu(\text{C=O})$
PAA	1710 cm^{-1}
PAA-Zn	1552 cm^{-1}
PAA-Ca	1548 cm^{-1}
PAA-Al	1588 cm^{-1}

From the result of ICP-AES measurements metal ion contents in PAA-Zn, PAA-Ca and PAA-Al were 28.5wt%, 20.6wt% and 10.8wt%, respectively. Assuming that all metal ions in these PAA salts combine -COO^- , 78mol%, 86mol% and 64mol% carboxylic acids in samples combine the metal cations in zinc, calcium and aluminum salts, respectively. The results of FT-IR and ICP-AES indicate that all carboxylic acids do not combine metal cations, although metal ions, equivalent to carboxylic acids, were added. Hence, the part of the metal chlorides could not react with PAA and effused during the washing procedure of the precipitations.

The reason for presence of unneutralized carboxylic

acids is as follows. When the aqueous solution of AlCl_3 is added in the aqueous solution of PAA-Na, Al^{3+} ions form octahedral $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ complexes in aqueous solution, and then, hydrated $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ is well known to change to hydroxyaquoaluminum ions such as following equations.



It is considered that -COO^- reacted with H^+ generated by these reactions and reverted to -COOH . Same reactions may also occur in other systems.

Fig. 2 shows the WAXS intensity profiles for the films of PAA and of PAA metal salts. No sharp reflection due to inorganic salts as impurities in specimens was observed. It is found that every salt did not crystallize and showed characteristic amorphous patterns depending on the kinds of metal ions. And the patterns of the PAA metal salts differ from that of PAA, meaning occurrence of a considerable conformational change of the molecular chains.

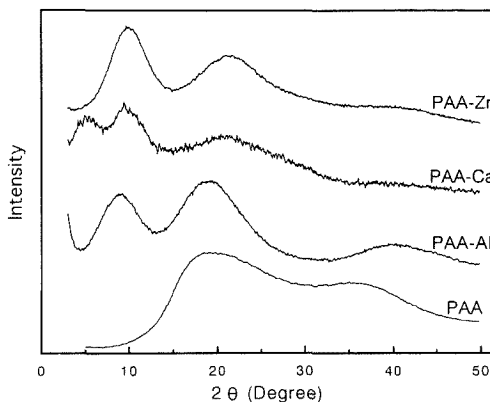


Fig. 2 Wide angle x-ray scattering profiles for PAA and its metal salts.

3.2 Mechanical properties and thermal behaviors of PAA metal salts

Fig. 3 shows temperature dependence of storage moduli (E') for the films of metal salts and PAA homopolymer. For unoriented polymeric materials, E' of Zn, Ca and Al salts are very high and are much higher than that of PAA. E' of PAA-Zn and PAA-Ca were over 20 GPa at room temperature. Especially, E' of Zn salt remained 20 GPa at 200°C and PAA-Ca exhibited E' of 7 GPa even at 400°C . High modulus and high heat

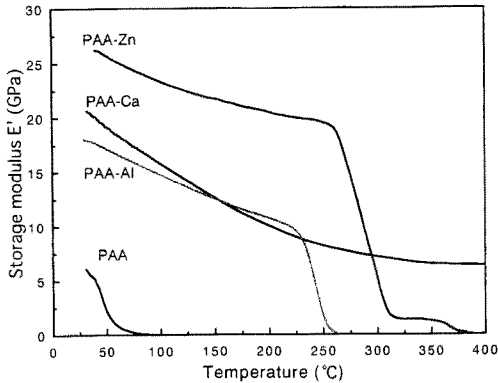


Fig. 3 Temperature dependence of storage moduli E' of PAA and its metal salts.

resistance of these specimens are attributed to Coulomb force between $-\text{COO}^-$ and multivalent metal ions.

It is, however, found that E' of PAA-Zn and PAA-Al decreased abruptly above 270°C and 220°C , respectively. Next, TG-DTA measurements were carried out to clarify the reason for decrease of E' for PAA-Zn and PAA-Al. Fig. 4 represents the TG-DTA thermogram for the film of PAA-Zn. From the TG-DTA curve the weight loss and sharp endotherm of a specimen occurred at 250°C . The weight loss above 250°C indicates the evolution of gas from the specimen and this would cause the abrupt decrease of E' . This temperature is lower than onset temperature of abrupt decrease of E' by 20°C , because for the smaller specimens for TG-DTA it is easy to conduct heat in the specimens and the component caused weight loss is easy to be excluded. Practically, the evolution of gas from the specimen for E' measurements was observed at 250°C

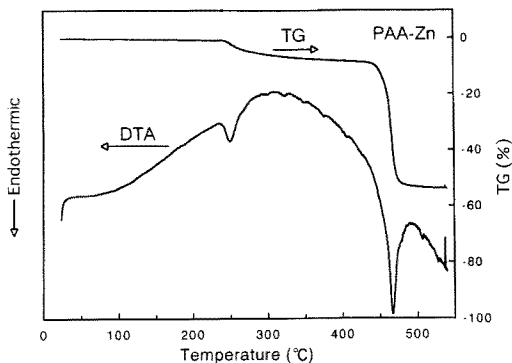


Fig. 4 TG-DTA thermogram for PAA-Zn salt.

for a few minutes.

Fig. 5 shows TG-DTA thermograms for the films of PAA-Ca and PAA-Al. The DTA thermogram of PAA-Al exhibited a sharp endothermic peak at about 220°C as well as that of PAA-Zn shown in Fig. 4. The thermal behavior of the PAA-Al salt in Fig. 5 also corresponds to the result from temperature dependence of E' for PAA-Al. Whereas, in the case of PAA-Ca the DTA thermogram gave a broad endothermic peak in the range of about 120°C to 250°C .

Fig. 6 shows the SEM images of the surface and fractured cross-section of PAA-Zn and PAA-Ca heat-treated at 250°C for 10 min. After heat treatment the features of specimens quite differ each other. That is to say, PAA-Zn had large cracks on the surface and a porous internal structure. On the other hand, PAA-Ca had a smooth surface and a densely internal structure. Judging from the results of TG-DTA and the SEM images, the gas evolves in PAA-Zn and PAA-Al above 200°C and forms many voids in the specimens, lead to cracks and abrupt decrease of E' . While PAA-Ca has no void though the weight loss occurs above 120°C . This means that the gas evolves gently from lower temperature than those of other salts and lead PAA-Ca to no cracks and no abrupt decrease of E' . We next measured the GC-MS to analyze the gas evolved at a

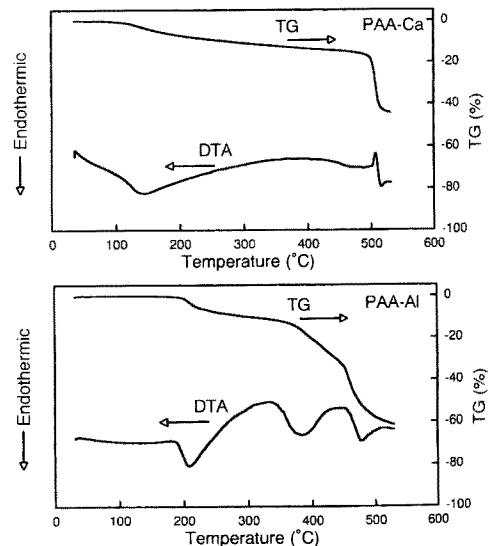


Fig. 5 TG-DTA thermogram for PAA-Ca and PAA-Al.

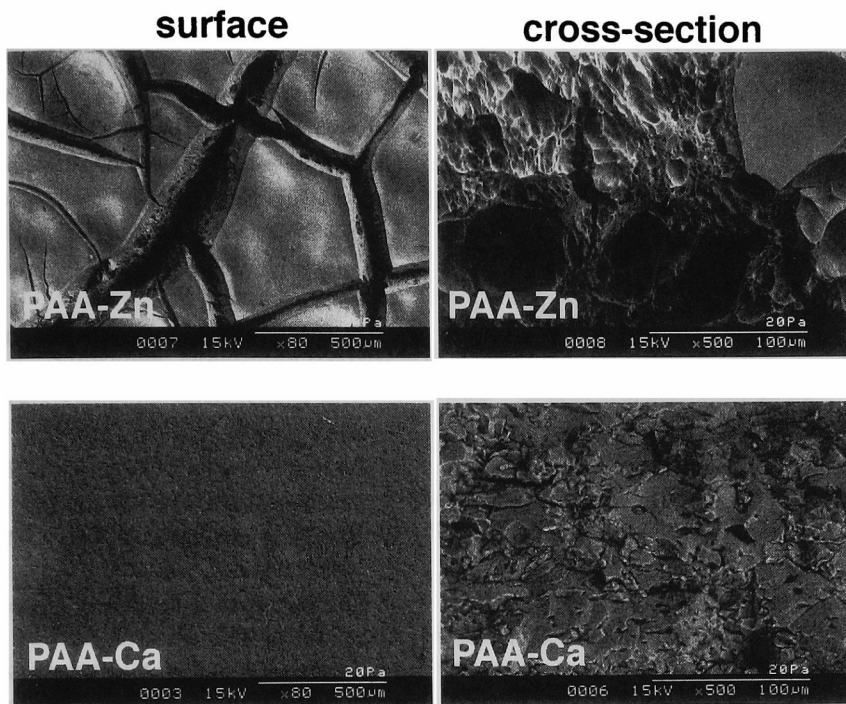


Fig. 6 SEM images of the surface and fractured cross-sectional view of PAA-Zn and PAA-Ca heat-treated at 250°C for 10min.

high temperature.

Fig. 7 shows mass spectra of GC-MS for PAA-Zn, PAA-Ca and PAA-Al, which were pyrolyzed at 250 °C for 30 sec using He as a carrier gas. From the results of each spectrum, mass numbers of gases generated at 250 °C were almost 17 or 18 of m/z (1), and therefore it can be concluded that most of the evolved molecules were H_2O . This is supported by the result that the evolved gas changed the color of anhydrous cobalt (II) chloride from blue to pink, implying the formation of hexaaquacobalt (II) ion complexes.

Thus, we measured FT-IR to clarify the origin of H_2O generation. Fig. 8 shows FT-IR spectra for two PAA-Zn, where an upper curve and a lower one exhibit spectra of non heat-treated and heat-treated samples, respectively. Heat-treatment was carried out at 250 °C for 30 min until finishing the evolution of H_2O completely. Two spectra were almost coincident except for the slight decrease of absorbance around 3500 cm^{-1} of the heat-treated PAA-Zn. There is no new absorption peak in particular, implying that thermal decomposition and change of PAA molecules did not

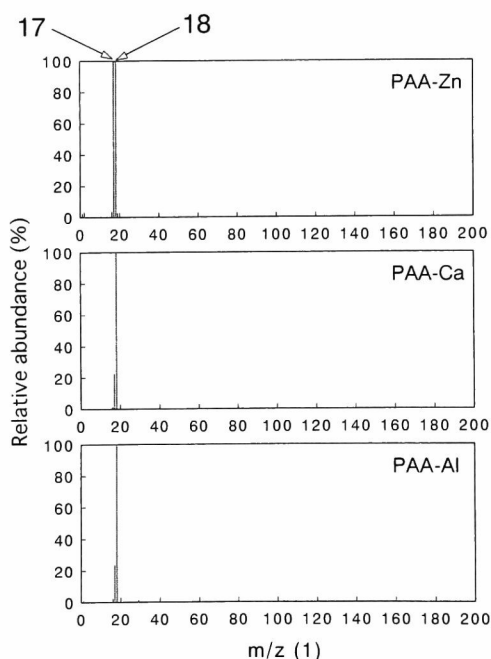


Fig. 7 Mass spectra for PAA-Zn, PAA-Ca and PAA-Al.

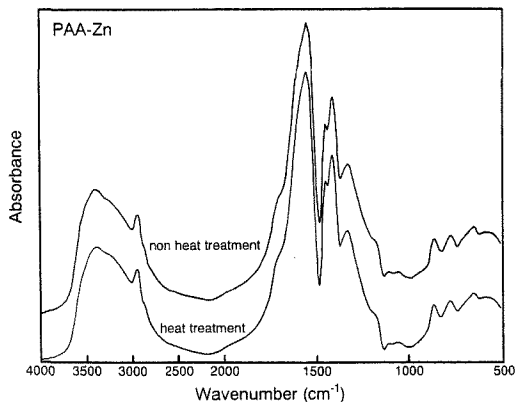


Fig. 8 FT-IR spectra for non heat-treated and heat-treated PAA-Zn. Heat treatment was carried out at 250°C for 30min.

occur by heat treatment. It is concluded that the slight decrease of absorbance around 3500cm^{-1} is attributed to the decrease of H_2O in the specimen, indicating the H_2O coordinated to metal ions.

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