Chapter IV

Experimental procedures

The extents of the present thesis

The present study was carried out to investigate the effect of metal salts on properties of PVA films containing metal salts by being focused on :

(1) An optimum condition for film preparation was investigated by varying features of metal salts, consuming times in preparing step, types of casting materials and temperature for film drying.

(2) Interaction or complex formation between the metal ions and the PVA molecules was investigated by using spectroscopic techniques such as UV-VIS, FTIR, ATR-FTIR, and Raman spectroscopy

(3) Environmental endurance of the PVA films were investigated in order to study effect of metal salts on PVA films. Resistance to solvent and water content including removed water under vigorous condition such as vacuum pressure, high temperature.

(4) Thermal properties influenced from metal were determined by dynamic mechanical spectroscopy (DMTA).

(5) Mechanical properties i.e. tensile strength, modulus of elasticity, strain to failure were carried out by using Lloyd 500 Universal Testing Machine.

(6) Effect of metal salt on morphology was illustrated by micrographs.

Objectives of the present studies is the effort to understand the effect of types and amount of metal on the properties of PVA films containing metal salts. Thus, the results should be essentially the informations for further investigations and difficulties. Every aspect of technical success and knowledges improvement may be carried out and created further success in the plastics industry.

Chemicals and materials

1. Polyvinyl alcohol (PVA)

The PVA used in the present study was PVA-120, a product of Kurare Co. Ltd. The PVA-120 is white powder having degree of polymerization (n) of 2000 and degree of hydrolysis of 98 mol%.

2. Metal salts and solvents

The metal salts used in the present study were metal chloride salts from the sources shown below.

Table 4.1 : Sources of metal chloride used in the present study.

No.	Metal salts	Sources
1	LiCl	Merck
2	NaCl	Farmitalia Carlo Erba
3	KCl	Kanto Chemical Co.,Inc.
4	$CaCl_2$	Kanto Chemical Co.,Inc.
5	$BaCl_2$	Kanto Chemical Co.,Inc.
6	$FeCl_2$	Kanto Chemical Co.,Inc.
7	$FeCl_3$	Kanto Chemical Co.,Inc.
8	$CuCl_2$	Kanto Chemical Co.,Inc.
9	$ZnCl_2$	Farmitalia Carlo Erba
10	$CoCl_2$	Kanto Chemical Co.,Inc.
11	$NiCl_2$	Kanto Chemical Co.,Inc.

The solvents used in the solvent resistance study were organic solvents from the sources shown below.

Table 4.2 : Sources of organic solvent used in the present study.

No.	Organic Solvent	Sources
1	Acetic acid	Farmitalia Carlo Erba
2	Chloroform	Farmitalia Carlo Erba
3	Methanol	Farmitalia Carlo Erba
4	Toluene	Farmitalia Carlo Erba
5	Xylene	Farmitalia Carlo Erba

Apparatus and instruments

Table 4.3 : Sources of the apparatus and instruments for this works

No.	Apparatus and Instruments	Sources
1	Water Distillation Apparatus	Büchii Fontavapor 210
2	Autodessicator	Eyela
3	Electronic Balance	Shimadzu, Libror Ael-40SM
4	Oven	Eyela
5	Vacuum Oven	
6	UV-Visible Spectrophotometer	Hitashi, U-2000
7	FTIR Spectrophotometer	Perkin-Elmer system 2000
8	ATR-FTIR Spectrophotometer	Perkin-Elmer system 2000
9	Raman Spectrophotometer	Perkin-Elmer system 2000
10	DMTA analyzer	Polymer Laboratory system MKII
11	Universal Testing Machine	Lloyd 500
12	Optical microscope	Olympus reflected microscope

Film formation optimization

1. Appropriate concentration for film preparation

Various concentrations of PVA solution were prepared by dissolving 1,5 and 10 % by weight of PVA powder, respectively, in deionized water and stirring overnight. Each solution was then casted on glass disc to obtain a PVA film.

The optimum concentration was also used for preparing metal salt containing PVA films.

2. Appropriate materials for film casting

Interfacial adhesive force between the resulting film and casting materials was used as a criteria for choosing appropriate materials for film casting. PVA films containing each metal salt were separately casted on glass disc, stainless steel disc, ceramic disc, teflon pan, PS sheet, PVC sheet, PMMA sheet, PE sheet and aluminium foil. Peeling capacity of each film was comparatively investigated.

3. Homogeneous distribution control of salt in film

PVA films containing metal salt were prepared by mixing each metal salt in PVA aqueous solution either as powder or as aqueous

solution of each salt. Homogeneous distribution of each salt in the resulting film was comparatively investigated.

In case of mixing the salt as aqueous solution, dependence on sequence of mixing was also investigated.

4. Thickness regularity control of PVA film

Regularity of film thickness was expected to depend on film casting temperature. Thus, PVA films were prepared by casting at various temperatures and distribution of the resulting films determined with micrometer.

5. Time for complex formation

It was expected that stirring time for mixture of metal salt and PVA solution should be one of the main factors affecting the formation of polymer-metal complex. Thus, PVA films containing metal salt were prepared with various stirring time and UV-VIS absorption at a specific wavelength of each film was comparatively investigated.

Preparation of PVA films containing metal

PVA films containing metal salt were prepared by using the optimum condition chosen from previous section; film formation optimization. Stock solution of 5 % by weight PVA was firstly prepared, then a portion of the PVA solution was mixed with various concentrations of LiCl, NaCl, KCl, $CaCl_2$, $BaCl_2$, $FeCl_2$, $FeCl_3$, $CuCl_2$, $ZnCl_2$, $CoCl_2$ and $NiCl_2$. The mixtures were stirred at ambient condition at least six hours, then casted on PE sheet and further dried at ambient temperature in an autodessicator for 2-3 weeks.

Investigation of metal-PVA interaction

1. **Property determination of film by spectroscopic techniques**

1.1. Ultraviolet-visible absorption measurement

Effect of types and amount of metal on film properties were determined by using Hitachi spectrophotometer U-2000 with scanning wavelength of 190 to 800 nanometers and scan speed of 200 nanometers per minute. Change in absorption spectra of each film was investigated by using the spectra of PVA film as a standard spectra.

1.2. Infrared absorption measurement such FTIR, ATR-FTIR, and RAMAN techniques

Infrared spectra of metal containing PVA films and PVA films standard were determined at ambient condition, by using Perkin-Elmer system 2000 fourier transform spectrophotometer at wavenumber of 360 - 4000 per cemtimeter. Attenuated total reflectance (ATR) technique was used to obtain the infrared spectra at wavenumber of 600-4000 per centimeter by using Perkin-Elmer system 2000 with zinc cyanide crystal holder having dimension of 0.8x7 cemtimeter and then, the Raman spectra were measured to confirm all of these spectra by using Perkin-Elmer system 2000 at wavenumber of 200-3600 per centimeter, 200-400 Hertz of x-ray radiation with 40 cycle times.

2. Environmental endurance investigation

PVA films containing metal salt are supposed to be used in various applications. Before designing for any application, the films should be tested for environmental endurance. Such environmental endurances are moisture absorption, chemical and/or solvent resistance, stress resistance, thermal resistance and so on.

Due to metal salts used in the present study are water soluble, the PVA films containing such a salt are supposed to be moisture sensitive. Thus, moisture content, water and/or organic solvent absorption, thermal properties and tensile properties were investigated.

2.1. Determination of moisture content

After each film was dried in an oven at 80 °C for 6 hours, it was further dried again in the oven at 100, 150 and 200 °C for 6 hours, 6 hours and 6 hours, respectively. Then weight of each film was respectively determined and percentage of eliminated water at each condition was calculated.

In addition, the films dried at 80 °C for 6 hours were also treated in an vacuum oven at 25 psi, room temperature for 48 hours and then percentage of eliminated water was determined.

2.2. Determination of water swellability

After the films were dried at 80 °C for 6 hours, the weight of each film was determined. Then each film was separately swollen in deionized water until equilibrium and the weight was determined. Percentage of water swelling for each film was calculated.

2.3. Determination of solvent swellability

The experiment was done as same as 2.2, but using chloroform instead of deionized water.

2.4. Determination of solvent resistance at ambient condition

The experiment was done as same as 2.3 but varying solvent such as chloroform, toluene, xylene, acetic acid and methanol. Each film was soaked in each solvent for 48 hours at ambient condition before solvent swellability was determined.

2.5. Determination of solvent resistance at vigorous condition

The experiment was done as same as 2.4 but vigorous condition of stirring at 100 °C for 6 hours. Dissolving or swelling of the films was investigated.

3. Thermal properties determination techniques

Thermal properties of PVA films containing metal salt and standard PVA films were comparatively investigated by using dynamic thermal analysis (DMTA) at temperature ranging from -20 ^{o}C upto 100 ^{o}C . Bending mode with frequency of 1 Hertz, 4 times strain, 1-4 strain level, and 2.8-3.4 power head range was used for the present study.

4. Mechanical property determination

Mechanical properties of PVA films containing metal salt and standard PVA film were comparatively investigated by using Lloyd 500 Universal testing machine. Tensile mode with six-bar pneumatic grips was used for the present study. The testing condition was used according to ASTM D-638 and ASTM D-882. Then the data was analyzed with Lloyd Dapmat version 2.2 and version 3.2.

5. The microscopic examination

The studies of light microscope provide an advantage of detail arrangement and location relationships within the metal contained PVA films specimens. Alignment and texture of the films samples was examined by using Olympus reflected-light microscope with expansion power being 100x10x1.25 times.

The suitable magnification was selected to obtain the required enlarged view. The coarse and fine adjustments were required as necessary to obtain the obvious image of metal through the scope. The photographs were then taken by a camera attached.