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The modification of ABS resin by introducing metal salts of unsaturated acids

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Graft polymerization of methacrylic acid onto ABS resin was carried out using BPO as an initiator in THF solution. Degree of grafting increased with reaction time and reached 35% in 10 hrs. Carboxyl groups were converted to carboxylates (metal salts) by refluxing MAA-g-ABS and the metal acetate in THF. In the solid graft polymers in solid, the infrared absorption of the asymmetrical C=O vibration of the carboxylic acid shifted to lower wavenumbers with increasing metal ion concentration. The absorption peak for the carboxylate anion is shifted to higher wavenumbers with the increase of alkali metal ion concentration, however, for the Mg^{2+} salt, it is shifted to lower wavenumbers. The surface and volume resistivities of the K^+ and Na^+ salts of MAA-g-ABS were $9.0 \times 10^9\ \Omega/\square$ and $9.5 \times 10^9\ \Omega$ at 80% neutralization, respectively, and decreased with alkali metal ion concentration. The electric resistance of Li^+, Mg^{2+} and Zn^{2+} salts decreased only slightly. The modulus of the K^+ salt of MAA-g-ABS decreased with neutralization, whereas in Li^+, Mg^{2+} and Zn^{2+} salts, the modulus increased with increasing metal ion concentration.

1. Introduction

Acrylonitrile-Butadiene-Styrene resin (ABS resin) is widely used in electric appliances and electronic apparatuses because of its excellent properties in electrical insulation, stiffness and impact resistance [1].

At the same time, electrostatic shock caused by contact with the other materials is a severe problem remaining to be resolved. Generally antistatic properties may be improved by adding substances of lower molecular weight to a polymer, which can, however, result in durability and mechanical strength problems. Recent research is directed not to "physical mixing" but to "chemical bond formation" of polar monomer or polymer molecules with the parent polymer chains by block or graft copolymerization [2–6]. The ionomer, in which ionizable groups such as metal or ammonium salts of sulfonic acids and carboxylic acids are introduced in hydrophobic polymers, are less hygroscopic than the parent polymer.

In this work, ionomers were prepared by introducing some metal salts of methacrylic acid onto ABS resin by graft polymerization, and the antistatic effects and mechanical properties were examined. The relationship of these properties with structural changes in the polymer caused by introducing ionizable group is also discussed.

2. Experimental

2.1. Materials and sample preparation

ABS resin (NP-10) was supplied from JSR Co. Ltd. Methacrylic acid (MAA) was purified by distillation under reduced pressure. Benzoyl peroxide (BPO) was recrystallized from chloroform. Commercially obtained THF of special grade and metallic acetates were used without further purification.

MAA and then BPO were added to a THF solution in which ABS resin was preliminarily dissolved under a nitrogen atmosphere at 60°C. After the graft polymerization reaction was finished, the reaction products were poured into water, and the precipitated graft polymer (ABS-g-MAA) was filtered.

The graft polymer and metal acetates were dissolved in THF, and were refluxed at 60°C. After about 6 hr the solvent was removed, and the remaining solid was compressed using a hot press at 10 MPa and 160°C for 5 min. Unreacted metal acetate was removed by extraction with hot water.

2.2. Measurements

For the purpose of determining the metal content of the ionomer, ICP measurements were carried out for samples of a hydrochloric acid solution. Each metal salt polymer was incinerated preliminarily at 700°C.

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Specimens for infrared spectroscopy were prepared by pressing each sample in a mould at 16 MPa and 160°C for 3 min. IR spectra were measured using a Nicolet N-750B spectrometer at room temperature, where 100 scans at a resolution of 4 cm^{-1} were averaged. The degree of grafting was estimated by the ratio of IR integrated peak area at 1700 cm^{-1} for the carbonyl(C=O) vibration of COOH against that at 2237 cm^{-1} for nitrile (C≡N) vibration.

The sheets for surface resistivity (ρ_S), volume resistivity (ρ_V), tensile testing and moisture absorption measurements were prepared by pressing each sample in a mould at 16 MPa and 160°C for 3 min.

Surface resistivity and volume resistivity measurements of 120 mm × 120 mm × 1 mm sheets were done as 1 minute values at the 500 V tension by a high resistance meter of a Yokokawa-Hewlett-Packard YHP 4329A, under conditions of 23°C and 50% relative humidity for 24 hr.

"Dogbone" specimens for tensile strength testing were stamped out from 1 mm thick sheets with JIS-3 dumbbell and were tested by using an Orientic tensilon RTA-500 at 23°C, with a crosshead speed of 50 mm/min, under the conditions of 23°C and 50% relative humidity for 24 hr.

The measurement of aqueous moisture permeability was carried out according to JIS Z 0208 as follows. A moisture permeation cup was covered with the sheet (120 mm^2 × 1 mm) to be tested. The relative humidity of the outside atmosphere was controlled at 90%, while the inside was kept dry by using a moisture absorbent. The permeability was estimated by the quantity of the steam which passed through this boundary surface per m^2 of the sheet material in 24 hr.

3. Results and discussions

Fig. 1 shows the change of extent of grafting initiated by BPO in THF. The reaction solution of 2.06 mol dm^{-3} of BPO reached 36.6% grafting in 10 hr. As shown in Fig. 2, the grafting increased exponentially with increasing BPO concentration.

The FT-IR spectra of parent ABS and a polymer 18% grafted with MAA are shown in Fig. 3, where a strong absorption due to the asymmetrical C=O vibration (ν_{as} C=O) of —COOH of MAA appears at 1704 cm^{-1}. Fig. 4 shows the change in the FT-IR spectra with ionomer concentration, in which the molar ratio was denoted as [added potassium acetate] / [MAA in graft polymer]. With increasing molar ratio, the peak intensity at 1704 cm^{-1} due to ν_{as} C=O of —COOH decreased and that of the —COO^- ion at 1550 cm^{-1} increased accordingly. However, the decreasing rate at 1704 cm^{-1} became much lower above 0.5 molar ratio.

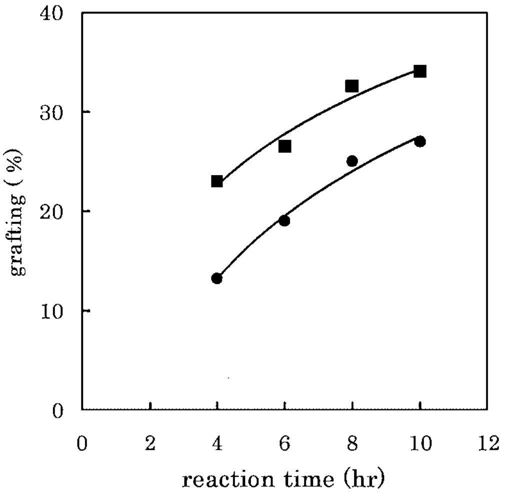


Figure 1 Effect of reaction time on the extent of grafting in THF at 60°C. ABS; 25 g, MA; 12.5 g, THF; 100 ml, BPO(mmol/l); ● 1.03, ■ 2.06.

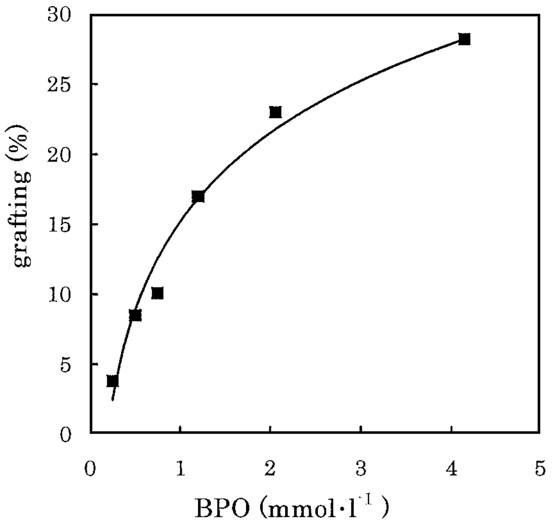


Figure 2 Effect of initiator content on the extent of grafting in THF at 60°C.

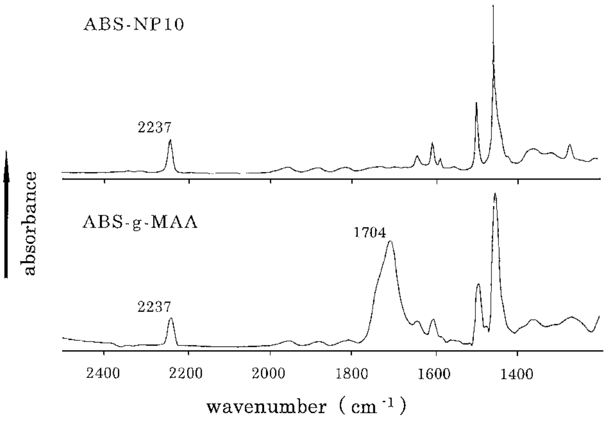


Figure 3 FT-IR spectra of ABS resin and ABS-g-MAA (grafting; 18%).

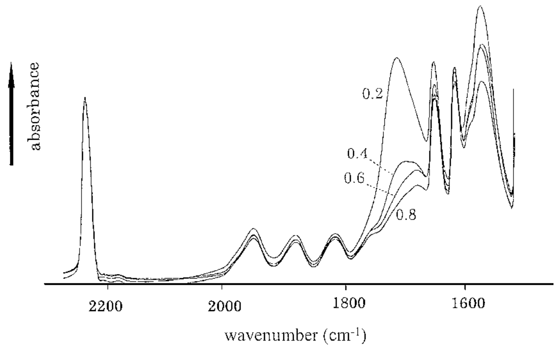


Figure 4 Change of Ft-IR spectra in the 1500–2300 cm^{-1} range of the potassium salt of ABS-g-MAA at various degrees of molar ratio.

The degree of conversion from —COOH to metal salt —COO^- M^+ increased linearly with increasing metal acetate concentration as shown in Fig. 5. That tendency was found in both Li^+ and K^+ ionomer formations.

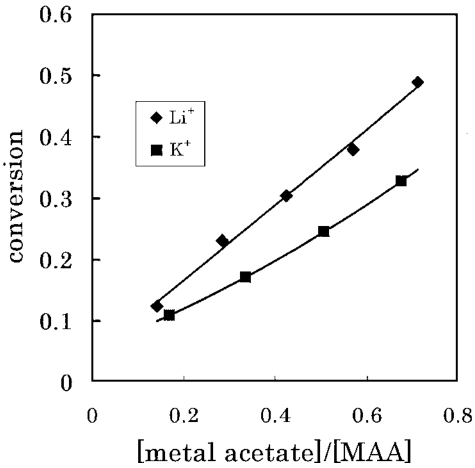


Figure 5 Relationship between conversion and molar ratio of metal acetate/MAA in ABS-g-MAA (grafting 18%).

After removing excess acetate, the IR spectra of the isolated ionomer were recorded. The FT-IR absorption peak due to carboxylic acid at 1700 cm^{-1} was shifted to the lower wavenumbers with increasing molar ratio of added potassium acetate in preparing the ionomer as shown in Fig. 6, in which abscissa represents the metal acetate concentration used when the MMA grafted polymer is converted to ionomer. The peak changed significantly for K$^+$, Na$^+$ and Mg^{2+} salts, from 1700 to 1670 cm^{-1}, whereas Li$^+$ salt did not change so much, only from 1700 to 1690 cm^{-1}. The force constant of the C=O vibration is lowered by introducing metal ion nearby carboxylic acid group: this is suggested by the fact that the degree of shift caused by interaction of carboxyl group and metal ion is related to bond enthalpy [7]. In the Li$^+$ salt ionomer, Lewis acid-base interaction between Li$^+$ and carboxylic acid is weak, because the acid strength of Li$^+$ is weaker than that of Na$^+$ and K$^+$ [8]. Therefore, the force constant, $k_{c=o}$ of MAA$^-$ Li$^+$ is larger than that of MAA$^-$ K$^+$, resulting in the smaller shift of Li$^+$ salt.

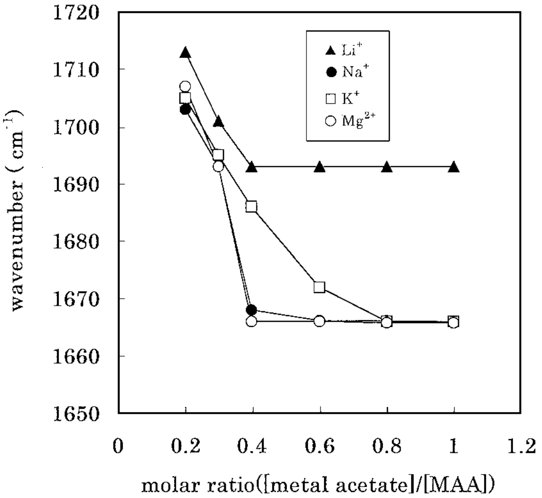


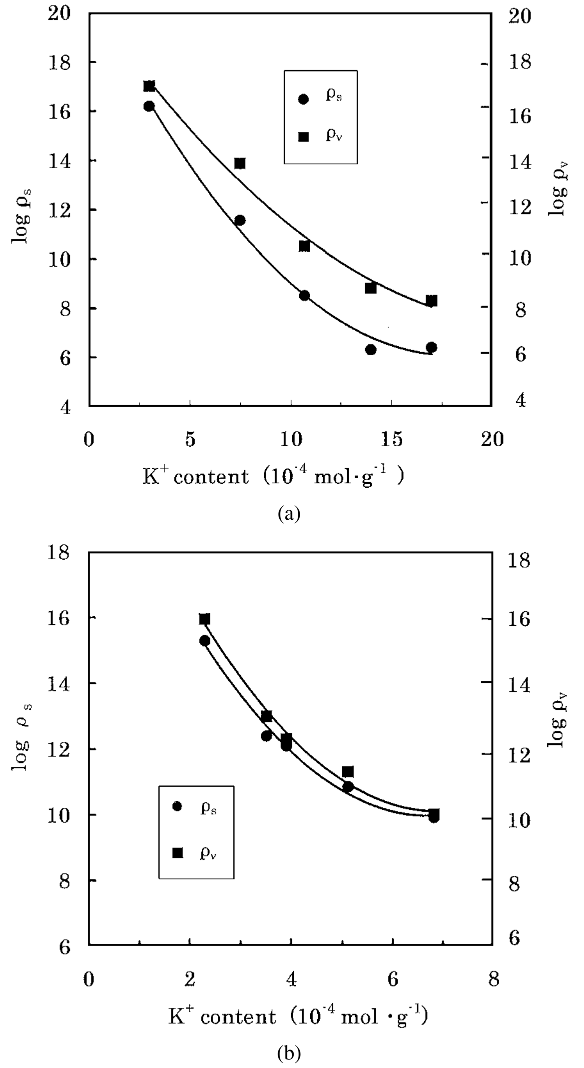
Figure 6 The FT-IR peak shifts with molar ratio for ABS-g-MAA modified samples in the region of 1700 cm^{-1}.

TABLE I Changes in the FT-IR peak shifts of ABS modified samples in the region of 1550 cm^{-1} with changing molar ratio

Molar ratio $\left(\frac{\text{Metal acetate}}{[\text{MAA}]}\right)$	Li$^+$ salt (cm^{-1})	Na$^+$ salt (cm^{-1})	K$^+$ salt (cm^{-1})	Mg^{2+} salt (cm^{-1})
0.2	1555	1549	1554	1549
0.3	–	1551	–	1545
0.4	1560	1552	1556	1539
0.6	1561	1552	1557	1539
0.8	1561	1552	1557	1539
Shift value	6	3	3	−10

Grafting 18%.

Similarly, the absorption peak for the carboxylate anion around 1550 cm^{-1} was shifted with the change of molar ratio of added acetate at the point of preparation, as shown Table I. In alkali metal salt ionomers, the peak was shifted to slightly higher wavenumbers with the increase of the molar ratio, whereas in the Mg^{2+} salt ionomer the shift occurred to lower wavenumbers and the degree of shift was larger than that for the alkali metal ionomers. In alkali metal salt ionomers, it seems likely that carboxylate groups are linked to neighboring carboxylate ions in *the same polymer* by electrostatic interaction through the metal ion. So the force constant is expected not to markedly change even with increasing metal ion concentration, which results in the only small shift of the IR peak. The thermal motion of grafted



(a)

(b)

Figure 7 (a) Variation of electrical resistance of ABS-g-MAA ionomer with the extent of K$^+$ content (before extraction). ■ ρ_S/Ω, ● $\rho_V/\Omega\cdot$cm. (b) Variation of electrical resistance of ABS-g-MAA ionomer with the extent of K$^+$ content (after extraction). ■ ρ_S/Ω, ● $\rho_V/\Omega\cdot$cm.

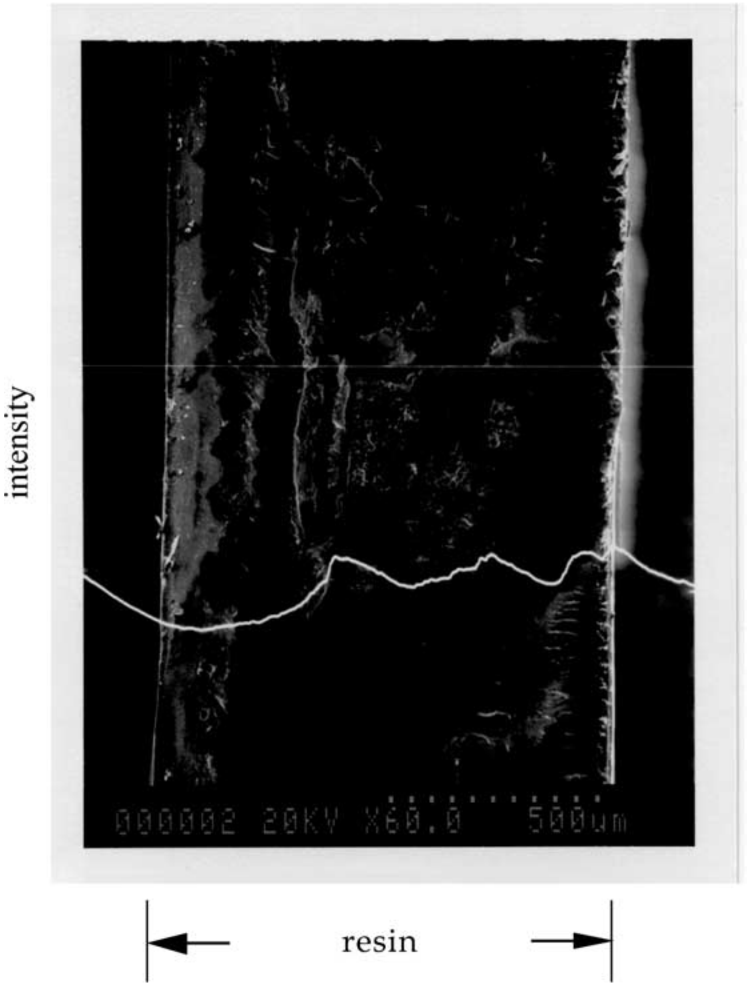
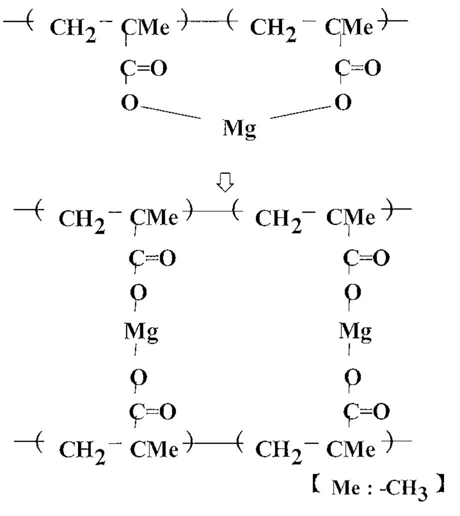


Figure 8 The EDX analysis of the potassium ion for unextracted ionomer.

chains is restricted locally due to intramolecular ring formation in *one polymer molecule*.

On the other hand, in the presence of Mg^{2+}, a polar carboxylate group in one grafted MAA polymer chain may be crosslinked intermolecularly through the Mg^{2+} with carboxylate groups in *different polymer molecules* (see Scheme 1). So the force constant $k_{c=o}$ of a carboxylate is expected to increase with increasing metal ion concentration, which results in the shift of the IR peak to higher wavenumbers. The interaction with Mg^{2+} may be primarily complex formation in which several carboxylate groups of *different polymers* are coordinated to a Mg^{2+} ion. Then the degree of freedom of a chain structure will be larger than that of a ring structure formed in the case of alkali metal ionomers.



Scheme 1 Intermolecular closslink through Mg^{2+} with carboxylate groups.

Electrical resistivity was examined for the ionomer samples with and without the metal acetate added at the preparation of the ionomer. Fig. 7a shows the change of surface(ρ_s) and volume(ρ_v) resistivities with K^+ content when the unreacted metal acetate is not removed. The resistivities ρ_s and ρ_v change differently each other. On the contrary when the unreacted metal acetate is removed by extraction ρ_s and ρ_v change similarly with K^+ content as shown in Fig. 7b. So K^+ ion which is not bound to carboxylate group of ionomer contributes to electric surface conductivity of the resin. However, the analysis of the K^+ ion for the potassium-unextracted polymer by EDX (Fig. 8) showed that the K^+ ion was not localized on the surface. Therefore, lowering of surface resistivity cannot be caused by the migration of metal ions but by the effect of water which is absorbed on the ionomer surface.

Figs 9 and 10 show changes in moisture permeability and volume resistivity with added cation content at the point of preparation of the ionomer. In the K^+ and Na^+ ionomers, the moisture permeability increased rapidly, and the volume resistivity decreased remarkably, whereas in the Li^+ and Mg^{2+} ionomers those showed only a slight dependence on cation content.

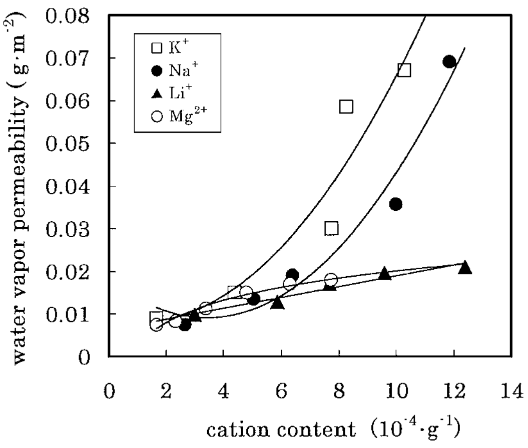


Figure 9 Variation of water vapor permeability of the ABS-g-MAA ionomer with extent of cation content.

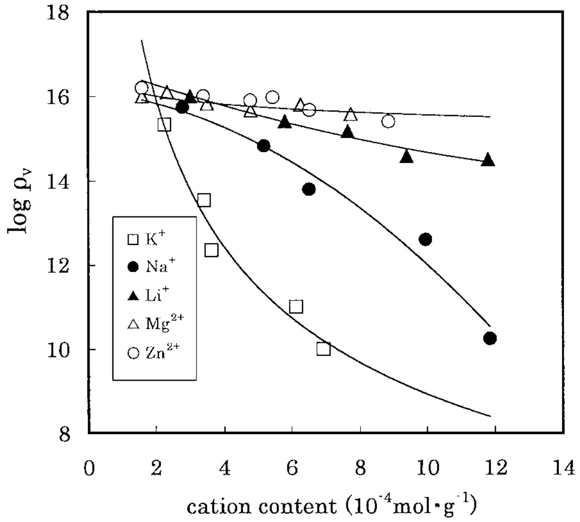


Figure 10 Volume resistivity of the ABS-g-MAA ionomer with extent of cation content.

Since electrical resistivity is related to hydrophilicity, i.e., the affinity of ionomers for water, relationship with aqueous moisture permeability was also examined. Fig. 11 shows that the higher value of volume resistivity (ρ_V) corresponds to the higher water vapor permeability regardless of metal ions of ionomers. It is concluded that the decrease of the volume resistivity in the ABS ionomers is controlled by the hygroscopicity.

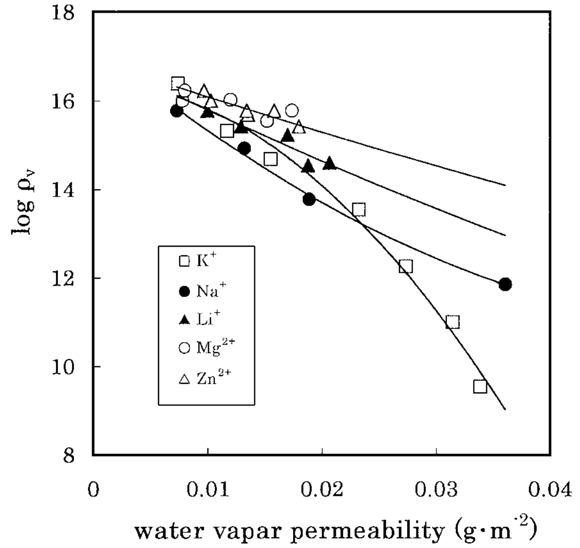
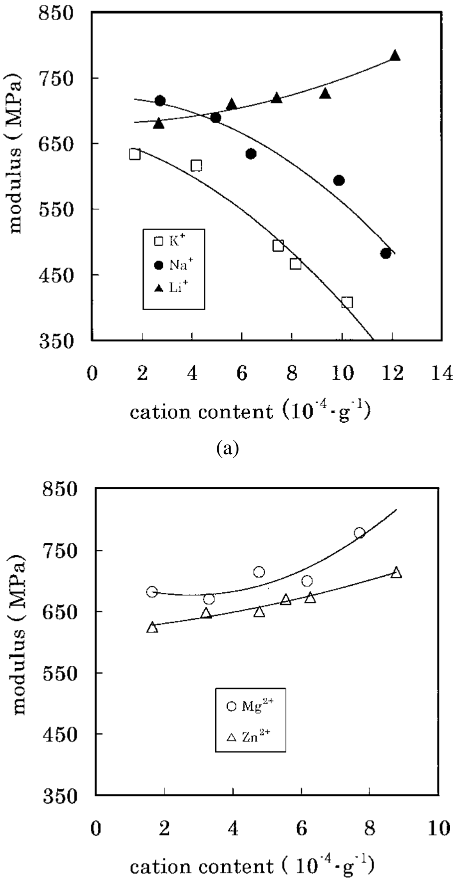


Figure 11 Variation of volume resistivity in ABS-g-MAA ionomer with the extent of water vapor permeability.



(a)

(b)

Figure 12 (a) Variation of modulus in ABS-g-MAA ionomer with the extent of cation content. (b) Variation of modulus in ABS-g-MAA ionomer with the extent of cation content.

In order to know applicability of these polymer resins modified to ionomers both mechanical and electrical properties were investigated. Fig. 12a shows that the modulus decreases for the K^+ and Na^+ salts, but changes little in Li^+ salt, with the increasing metal ion content. As discussed in the previous section, increasing cation content enhances aqueous moisture absorption, which may in turn generate plasticization. On the other hand, in Mg^{2+} and Zn^{2+} salt ionomers the modulus increased with the metal ion content as shown in Fig. 12b. The increasing modulus with the metal ion content can be related with the progressing of the complex formation reaction between intermolecular carbonyl groups through the bivalent cation. In K^+ and Na^+ salt ionomers with the high hygroscopic ability, however, the increasing modulus is ascribed to the role of the absorbed water. These water molecules are settled near the polar groups at grafted side chains, strongly coordinate around the small univalent cations, and so inhibit the crosslinking formation between intermolecular carbonyl groups through the univalent cation.

4. Conclusions

In graft polymers containing ionic polar groups, the absorption peak of C=O of carboxylic acid was shifted to lower wavenumbers with increasing metal acetate concentration used. This shift may be caused by the Lewis acid-base interaction at the bonding sites between carboxylic acid and alkali metal ion.

Carboxylate anions in alkali metal salt ionomers can be linked, due to predominantly electrostatic interaction through the metal ion, with neighboring carboxylate ions in *the same polymer*. That was reflected on the slight peak shift to higher wavenumbers with the increasing cation content. On the other hand, in the Mg^{2+} salt ionomer the shift occurred to lower wavenumbers and the degree of shift was considerably larger than that for alkali metal ionomers. In the presence of Mg^{2+}, a polar carboxylate group in one grafted MAA polymer chain may be crosslinked intermolecularly through the Mg^{2+} with carboxylate groups of a *different polymer molecules*.

Water molecules were absorbed onto the resin surface, when the graft polymer was converted to ionomer. That water enhanced greatly the electrical conduction in the K^+ and Na^+ salt ionomers, and lowered remarkably modulus and tensile strength. It was because the absorbed water might inhibit intermolecular complex formation, and promoted plasticization.

In Mg^{2+} and Zn^{2+} salt ionomers, the electric resistance was not lowered very much, and modulus increased with the increase in metal ion content.

References

1. R. B. SEYMOUR and G. S. KIRSHERBAUM, in "High Performance Polymers" (Elsevier, New York, 1986) p. 125.
2. J. R. ALLAN, J. G. BONNER and D. L. GERRARD, *Plastics Rubber and Composites Processing and Applications* **24** (1995) 43.
3. M. TELLEZ, F. RODRIGOUES, M. MONDRAGON and L. F. RAMOS, *SPE. ANTEC Tech.* **41** (1993) 237.
4. F. J. RODRIGOUES-GONZALES, L. F. RAMOS-DE VALLE and D. NAVARRO-RODRIGOUES, *SPE. ANTEC Tech.* **43** (1995) 2076.
5. H. XU and C. YANG, *J. Polym. Sci. Part B, Polym. Phys.* **33** (1995) 745.
6. K. H. LEE and J. K. PARK, *ibid.* **36** (1998) 991.
7. F. M. FOWKES and D. O. TISCHLER, *J. Polym. Sci. Part A, Polym. Chem.* **22** (1984) 547.
8. T. S. LEE, in "Treatise on Analytical Chemistry" Vol. 1, part. 1 (Interscience, New York, 1959) p. 185.

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