

Preparation and Copolymerization of Divalent Metal Salts of Ethylene Glycol-Methacrylate-Phthalate

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Synopsis

Divalent metal salts of ethylene glycol-methacrylate-phthalate (EMP) were prepared by the reaction of EMP and divalent metal ions in aqueous solution. The divalent metal salts obtained, except for the Pb salt, have melting points which decrease in the order of $\text{Ca} > \text{Ba} > \text{Mg} > \text{Zn} > \text{Cd}$ salt. The Zn and Cd salts are fairly soluble in most organic solvents. Therefore, the Zn salt and Cd salt were selected for the copolymerization with MMA, styrene (St), and hydroxyethyl methacrylate (HEMA). In the copolymerization, the rates of copolymerization increased markedly as the concentration of metal salts increased. Moreover, the systems containing MMA copolymerized more rapidly than those containing St. As for the physical properties of the copolymers obtained, compressive strength and Rockwell hardness were improved by introducing metal salts into the polymers; and heat distortion temperature and tensile and flexural strengths were also improved by selecting the most suitable concentration of metal salts according to the species of metal salts and vinyl monomers. The TGA and the boiling water resistance of the copolymers were also discussed.

INTRODUCTION

In recent years, many studies¹ have been made about polymers ionically crosslinked by metal ions, for example, studies on ionic crosslinking of diene polymer,² ethylene polymer³ (copolymer of ethylene with methacrylic or acrylic acid), and acrylate polymer.⁴ Especially, Surlyn A (ionically crosslinked polymer from ethylene polymer) has attracted a fair amount of interest from the scientific and industrial standpoint. It is generally known that by ionic crosslinking the tensile strength of these polymers is improved and, at the same time, remarkable effects on heat stability, durability, and resistance to water, alkali, and acid can be seen. The usual method of preparation of ionically crosslinked polymers is such that first a base polymer containing a functional group capable of forming an ionic crosslink, such as a carboxylic acid group at a side chain, is prepared, and then the polymer is neutralized with metal salts.

On the other hand, it is considered that by copolymerizing a polymerizable monomer already containing an ionic bond with vinyl monomers, an ionically crosslinked polymer will be obtained in one step. The ionically

crosslinked polymers prepared by such a method and the monomers suitable for this purpose are little known, so far as the authors are aware.

In the present study, as the polymerizable monomers containing an ionic bond, divalent metal salts (I) of EMP were prepared and were copolymerized with other vinyl monomers:



I

where M = divalent metal. The EMP can be prepared easily by the addition reaction of commercially available hydroxyethyl methacrylate (HEMA) and phthalic anhydride. Compound I was prepared by the reaction of EMP and divalent metal ions. MMA, styrene (St), and HEMA were used as vinyl monomers.

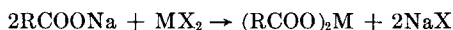
EXPERIMENTAL

Preparation of EMP

EMP was prepared by the reaction of HEMA and phthalic anhydride. The method of preparation was as follows: Into a three-necked flask, 843.4 g (6.5 moles) of HEMA, 888.7 g (6.0 moles) of phthalic anhydride, and 23.8 g (0.1 mole/kg) of N,N-dimethylbenzylamine were added and the mixture was stirred at 90°C for 5 hr. The acid value of the product (EMP) was 193.2 (calcd. 191.7). EMP was used without further purification.

Preparation of Divalent Metal Salts (I) of EMP

Method A:

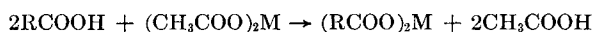


where X = Cl or CH₃COO.

Into a three-necked flask in which EMP was dispersed in large amounts of water with stirring, an aqueous solution of equivalent weight of Na₂CO₃ was added slowly at room temperature. As soon as the reaction began, CO₂ began to evolve from the mixture, and EMP was gradually converted into Na salt. After reaction, the pH of the aqueous solution was 7.0.

To the aqueous solution of Na salt of EMP prepared above, an aqueous solution of chloride or acetate of divalent metal equivalent to the amount of Na salt was added slowly at room temperature. As the reaction proceeded, metal salt precipitated in the form of white powder or milk-white viscous liquid. After reaction the product was washed with distilled water and dried in vacuo at room temperature.

Method B:



Into a three-necked flask in which EMP was dispersed in large amounts of water with stirring, an aqueous solution of equivalent weight of acetate of divalent metal was added slowly at room temperature. As the reaction proceeded, divalent metal salt precipitated in the form of a white powder. After reaction, the product was washed with distilled water and dried in vacuo at room temperature.

The bromine numbers of the products were determined according to the bromination method.⁵

Copolymerization of Compound I and Vinyl Monomers

The ampoule polymerization for determining the conversion in the copolymerization of compound I with MMA, St, and HEMA was carried out according to the usual method.

The method of preparation of resin boards for determining physical properties was as follows: To the mixture of I and vinyl monomers, 0.5 wt-% of 60% dimethyl phthalate solution of methyl ethyl ketone peroxide (MEKPO) and 0.5 wt-% of 10% styrene solution of cobalt naphthenate were added. After the atmosphere was replaced by nitrogen, the mixture was poured into molds consisting of two stainless boards laminated with Teflon sheets, separated by a rubber gasket and, after degassification, polymerized at fixed temperature for fixed period.

HEMA was used after distillation under reduced pressure. MMA and St of chemically pure grade were used without further purification.

Determination of Physical Properties

The heat distortion temperature (HDT) was determined in accordance with ASTM-D 648-56.

Tensile strength was determined in accordance with ASTM-D 638-64 T.

Flexural strength was determined in accordance with ASTM-D 790-63.

Compressive strength was determined in accordance with ASTM-D 695-63 T.

Impact strength was determined in accordance with ASTM-D 256-56 (with Izod notch).

Rockwell hardness was determined in accordance with ASTM-D 785-62 (M scale).

Thermogravimetric Analyses

Thermogravimetric analyses (TGA) were carried out in a thermo-balance TGA-20 of Shimadzu Seisakusho, at a heating rate of 5°C/min in air.

RESULTS AND DISCUSSION

Preparation of Compound I

As divalent metal ions, Mg, Ca, Zn, Cd, Ba, and Pb were selected. The results of the preparation of I are summarized in Table I. Compound I

TABLE I
Synthesized Metal Salts of EMP

| Metal | Expt. no. | Method of synthesis | Yield, % | Melting point, °C | Metal, % | | Bromine no. | |
|-------|-----------|---------------------|----------|-------------------|----------|--------|-------------|--------|
| | | | | | Found | Calcd. | Found | Calcd. |
| Mg | 1 | A ^a | 45 | 129-131 | 4.63 | 4.20 | 59 | 55 |
| Ca | 2 | A ^a | 89 | 204-205 | 6.84 | 6.74 | 54 | 54 |
| Zn | 3 | A ^a | 30 | | 10.85 | 10.54 | 58 | 52 |
| | 4 | B | 92 | 72-80 | 10.39 | | 50 | |
| | 5 | A ^b | 70 | 42-47 | 16.49 | 16.85 | 52 | 48 |
| | 6 | A ^a | 72 | | 16.16 | | 47 | |
| Ba | 7 | A ^a | 66 | 163-164 | 20.50 | 19.85 | 48 | 46 |
| Pb | 8 | A ^b | 81 | — | 28.25 | 27.20 | 40 | 42 |

^a MX₂ used was MCl₂.

^b MX₂ used was (CH₃COO)₂M.

TABLE II
Solubility of Metal Salts of EMP^a

| Solvent | Mg salt | Ca salt | Zn salt | Cd salt | Ba salt | Pb salt |
|---------------|---------|---------|---------|---------|---------|---------|
| Styrene | — | — | — | — | — | — |
| MMA | — | — | — | + | — | — |
| HEMA | — | — | + | + | — | — |
| Benzene | — | — | — | — | — | — |
| Methanol | + | — | + | + | — | — |
| Acetone | — | — | + | + | — | — |
| Dioxane | — | — | + | + | — | — |
| Ethyl acetate | — | — | + | + | — | — |
| Chloroform | +— | +— | + | + | +— | — |
| Ethyl ether | — | — | — | — | — | — |
| Water | + | — | — | — | — | — |

^a (+) Soluble; (+—) partially soluble; (—) insoluble.

can be prepared in aqueous solution generally with high yields. Since the metal salts, except for the Mg salt, are insoluble in water, they precipitated as white powders in water. The Pb salt, however, precipitated as milk-white viscous liquid. The Mg salt precipitated as white powder by cooling the solution after the reaction. Close agreement between experimental and calculated values of metal content of all products was obtained. When Zn salt was prepared by method A, the yield was low, and the experimentally determined bromine number is somewhat higher than the calculated value. But when it was prepared by method B, the yield was very high, and close agreement between the experimentally determined and calculated bromine numbers was obtained. Therefore, it is considered that the method suitable for preparing Zn salt is B-method.

The metal purified salts, except for the Pb salt, have melting points which decrease in the order of Ca > Ba > Mg > Zn > Cd salt. In the infrared spectra of the metal salts obtained, an absorption band about 1600 cm⁻¹, which is characteristic of carboxylate (antisymmetric stretching vibration) and cannot be seen in case of EMP is observed. This means that a static ionic bond between COO⁻ and M⁺⁺ is formed. Moreover, absorption bands about 1630 and 940 cm⁻¹, which are characteristic of the terminal vinyl group, are observed.

The solubility characteristics of the metal salts obtained are shown in Table II. The Zn and Cd salts are fairly soluble in chief organic solvents, but other metal salts are insoluble. In HEMA, the Zn and Cd salts are soluble. Therefore, the metal salts considered to be suitable for copolymerization are these two metal salts; besides, in the copolymerization, it is necessary that HEMA be used as one component of the comonomers.

The copolymerization of the Zn and Cd salts with MMA, St, and HEMA was then carried out. The Zn and Cd salts which were used in the copolymerization were prepared according to experiment no. 4 (method B) and experiment no. 6 (method A) in Table I, respectively. The Zn and

Cd salts will be denoted hereafter by $(\text{EMP}-)_2\text{Zn}$ and $(\text{EMP}-)_2\text{Cd}$, respectively ($\text{EMP}-$ means EMP residue).

Copolymerization

The solubilities of the metal salts in MMA and St are shown in Table II. However, it was found that by using the mixtures of these vinyl monomers and HEMA, homogeneous compositions for copolymerization could be obtained. That is, the mixture of MMA or St and HEMA in the ratio of 3.33:1 (by weight) dissolves $(\text{EMP}-)_2\text{Zn}$ and $(\text{EMP}-)_2\text{Cd}$ fairly readily. Therefore, in the mixtures of this constant ratio were dissolved the metal salts in various quantities and the compositions were copolymerized. However, since $(\text{EMP}-)_2\text{Cd}$ is soluble in MMA, in this case $(\text{EMP}-)_2\text{Cd}$ was copolymerized with MMA.

The time-conversion curves for the copolymerization are shown in Figures 1 and 2. In all systems, the rates of copolymerization increased markedly as the concentration of the metal salts increased. This tendency is a phenomenon characteristic of the divinyl compounds, namely, it is considered that, as the concentration of metal salts which are divinyl compounds increases, the viscosity of polymerization system increases, so that, by the so-called "gel effect," the rate of polymerization increases. Besides, the rates of polymerization of the systems containing MMA are much larger than those of the systems containing St, and at 55°C conversion reached nearly the maximum conversion attainable after 1-5 hr. In the systems containing St, when the concentration of metal salts was low, conversion did not reach the maximum conversion attainable even after 10 hr. Successively, the second-step polymerizations were carried out at 100°C, as a result, it was found that the conversion of slow poly-

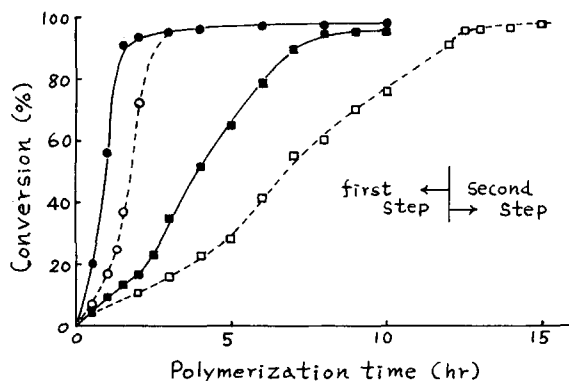


Fig. 1. Time-conversion curve for copolymerization of $(\text{EMP}-)_2\text{Zn}$ -vinyl monomers: (○) $(\text{EMP}-)_2\text{Zn}$ 5 wt-%, MMA-HEMA (3.33/1) 95 wt-%; (●) $(\text{EMP}-)_2\text{Zn}$ 20 wt-%, MMA-HEMA 80 wt-%; (□) $(\text{EMP}-)_2\text{Zn}$ 5 wt-%, St-HEMA (3.33/1) 95 wt-%; (■) $(\text{EMP}-)_2\text{Zn}$ 20 wt-%, St-HEMA 80 wt-%. First-step polymerization temperature 55°C, second-step polymerization temperature 100°C.

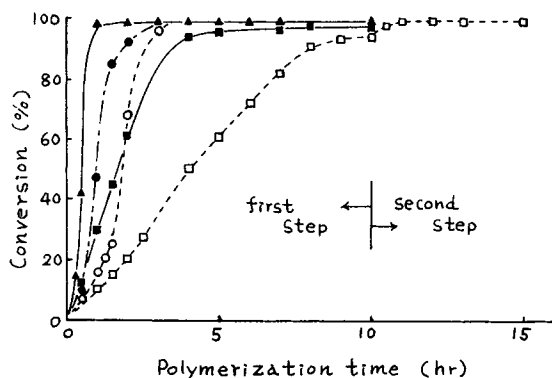


Fig. 2. Time-conversion curve for copolymerization of $(\text{EMP}-)_2\text{Cd}$ -vinyl monomers: (○) $(\text{EMP}-)_2\text{Cd}$ 10 wt-%, MMA 90 wt-%; (●) $(\text{EMP}-)_2\text{Cd}$ 20 wt-%, MMA 80 wt-%; (▲) $(\text{EMP}-)_2\text{Cd}$ 40 wt-%, MMA 60 wt-%; (□) $(\text{EMP}-)_2\text{Cd}$ 10 wt-%, St-HEMA (3.33/1) 90 wt-%; (■) $(\text{EMP}-)_2\text{Cd}$ 20 wt-%, St-HEMA 80 wt-%. First-step polymerization temperature 55°C , second-step polymerization temperature 100°C .

merization systems reached the maximum conversion attainable within 3–5 hr.

In all cases, the observed gelation of the polymerization systems occurred at 15–30% conversion. Moreover, at the beginning of the polymerization, the copolymer obtained contained a large quantity of chloroform-soluble part; but as the conversion increased, the chloroform-soluble part decreased markedly and became negligible above 50% conversion.

For obtaining homogeneous compositions for copolymerization, it is necessary to keep the concentration of the metal salts in the systems below about 20%, and that of $(\text{EMP}-)_2\text{Cd}$ in the $(\text{EMP}-)_2\text{Cd}$ -MMA system below about 40%. Among the copolymers obtained by the above polymerization conditions, those containing St were somewhat opaque, and those containing MMA were transparent.

According to the results of the copolymerization mentioned above, the polymerization conditions for obtaining samples for determining physical properties were as follows: first-step polymerization at 55°C for 10–12 hr; second-step polymerization at 100°C for 5 hr; further, third-step polymerization at 110°C for 2 hr.

Physical Properties of Copolymers

The compositions of the copolymers used for determining physical properties were as follows: in the copolymers of $(\text{EMP}-)_2\text{Cd}$ -MMA, the concentration of $(\text{EMP}-)_2\text{Cd}$ was up to about 40% (by weight); in the other copolymers, that of the metal salts was up to about 20%. The weight ratio of MMA or St and HEMA was 3.33:1.

Heat Distortion Temperature (HDT). As shown in Figure 3, in the copolymers of $(\text{EMP}-)_2\text{Cd}$ -MMA, HDT has a peak of 112°C at 10% $(\text{EMP}-)_2\text{Cd}$. In the other copolymers, HDT is not affected by metal

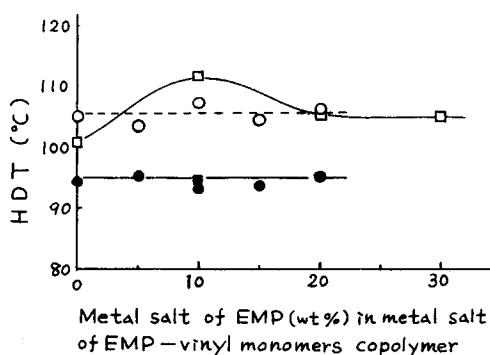


Fig. 3. Effect of metal salt of EMP on HDT of metal salt of EMP-vinyl monomers copolymer: (O) $(\text{EMP}-)_2\text{Zn-MMA-HEMA}$; (●) $(\text{EMP}-)_2\text{Zn-St-HEMA}$; (□) $(\text{EMP}-)_2\text{Cd-MMA}$; (■) $(\text{EMP}-)_2\text{Cd-St-HEMA}$. Weight ratio of MMA or St/HEMA = 3.33/1.

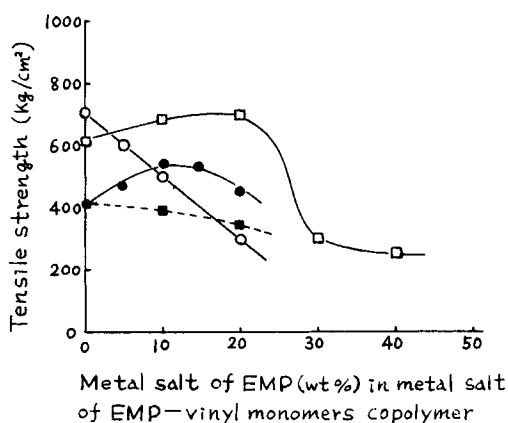


Fig. 4. Effect of metal salt of EMP on tensile strength of metal salt of EMP-vinyl monomers copolymer: (O) $(\text{EMP}-)_2\text{Zn-MMA-HEMA}$; (●) $(\text{EMP}-)_2\text{Zn-St-HEMA}$; (□) $(\text{EMP}-)_2\text{Cd-MMA}$; (■) $(\text{EMP}-)_2\text{Cd-St-HEMA}$. Weight ratio of MMA or St/HEMA = 3.33/1.

salts. When the copolymer of St-methacrylic acid (MAA)-ethyl acrylate (EA) was ionically crosslinked by the usual method, HDT increased markedly,⁶ but in the present copolymers containing St, such a tendency is not seen.

Tensile Strength. As shown in Figure 4, in the copolymers of $(\text{EMP}-)_2\text{Cd-MMA}$, tensile strength has a peak at 20% $(\text{EMP}-)_2\text{Cd}$. Further increase of $(\text{EMP}-)_2\text{Cd}$ reduces the tensile strength markedly. In the copolymers of $(\text{EMP}-)_2\text{Zn-MMA-HEMA}$, tensile strength decreases linearly with increase in $(\text{EMP}-)_2\text{Zn}$. The existence of peak values depends on the species of metal salts and vinyl monomers. On the other hand, there have been reports that ionic crosslinking of polystyrene, which is a representative amorphous polymer, showed little effect on tensile strength,⁷ and that in the glassy St-MAA-EA copolymer, tensile strength rather decreased as the degree of ionic crosslinking increased.⁶

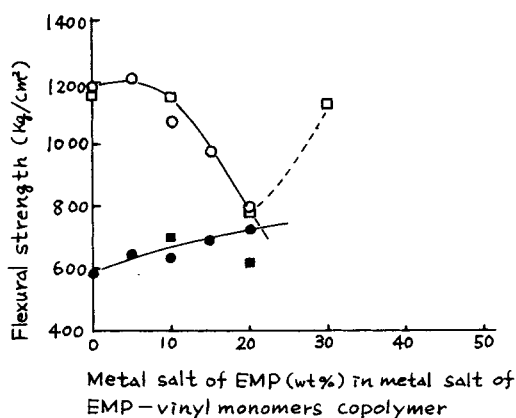


Fig. 5. Effect of metal salt of EMP on flexural strength of metal salt of EMP-vinyl monomers copolymer: (O) $(\text{EMP}-)_2\text{Zn-MMA-HEMA}$; (●) $(\text{EMP}-)_2\text{Zn-St-HEMA}$; (□) $(\text{EMP}-)_2\text{Cd-MMA}$; (■) $(\text{EMP}-)_2\text{Cd-St-HEMA}$. Weight ratio of MMA or St/HEMA = 3.33/1.

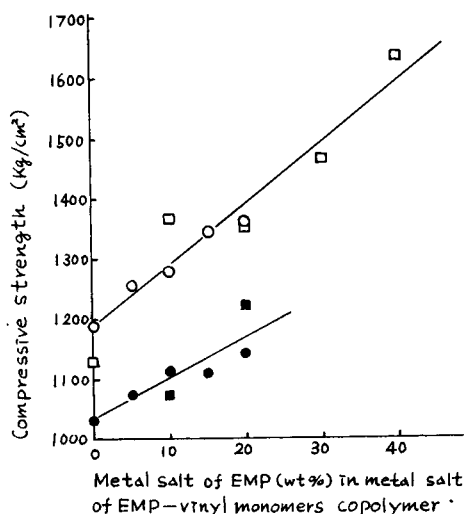


Fig. 6. Effect of metal salt of EMP on compressive strength of metal salt of EMP-vinyl monomers copolymer: (O) $(\text{EMP}-)_2\text{Zn-MMA-HEMA}$; (●) $(\text{EMP}-)_2\text{Zn-St-HEMA}$; (□) $(\text{EMP}-)_2\text{Cd-MMA}$; (■) $(\text{EMP}-)_2\text{Cd-St-HEMA}$. Weight ratio of MMA or St/HEMA = 3.33/1.

Flexural Strength. As is clear from Figure 5, in the copolymers containing MMA, in the region of 5–20% metal salts, flexural strength decreases markedly with increase in metal salt concentration. However, it is noteworthy that in the $(\text{EMP}-)_2\text{Cd-MMA}$ copolymers, flexural strength reaches the value of 1130 kg/cm² at 30% $(\text{EMP}-)_2\text{Cd}$. On the other hand, in the copolymers containing St, flexural strength increases gradually as the metal salts increase, and in this case the effect of introducing metal salts appears.

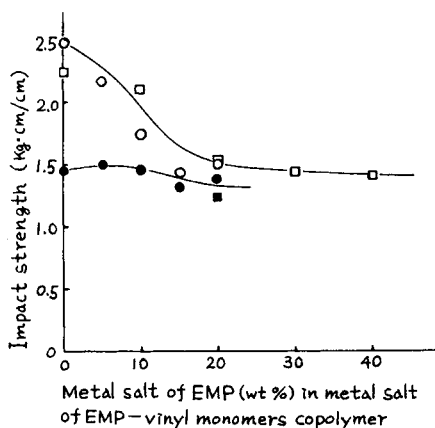


Fig. 7. Effect of metal salt of EMP on impact strength of metal salt of EMP-vinyl monomers copolymer: (O) $(\text{EMP}-)_2\text{Zn-MMA-HEMA}$; (●) $(\text{EMP}-)_2\text{Zn-St-HEMA}$; (□) $(\text{EMP}-)_2\text{Cd-MMA}$; (■) $(\text{EMP}-)_2\text{Cd-St-HEMA}$. Weight ratio of MMA or St/HEMA = 3.33/1.

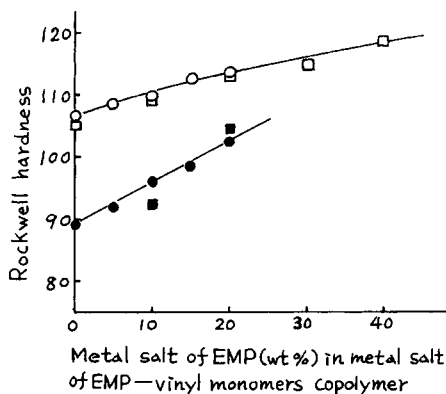


Fig. 8. Effect of metal salt of EMP on Rockwell hardness of metal salt of EMP-vinyl monomers copolymer: (O) $(\text{EMP}-)_2\text{Zn-MMA-HEMA}$; (●) $(\text{EMP}-)_2\text{Zn-St-HEMA}$; (□) $(\text{EMP}-)_2\text{Cd-MMA}$; (■) $(\text{EMP}-)_2\text{Cd-St-HEMA}$. Weight ratio of MMA or St/HEMA = 3.33/1.

Compressive Strength. As is clear from Figure 6, in all copolymers compressive strength increases almost linearly with increase in metal salt concentration. For instance, in the $(\text{EMP}-)_2\text{Cd-MMA}$ copolymers, compressive strength reaches the value of 1640 kg/cm² at 40% $(\text{EMP}-)_2\text{Cd}$. Thus, in compressive strength, the effect of introducing metal salts appears to be considerable.

Impact Strength. As shown in Figure 7, in the copolymers containing MMA, impact strength decreases with increase in metal salts up to 20% metal salts, above which impact strength remains nearly unchanged. On the other hand, in the copolymers containing St, a little decrease in impact strength is observed around 20% metal salts.

Rockwell Hardness. As shown in Figure 8, in all copolymers Rockwell hardness increases linearly as the metal salts increases; particularly, the rate of increase in the copolymers containing St is high. In Rockwell hardness, too, the effect of introducing metal salts appears to be marked. In summary, the following conclusions may be reached: compressive strength and Rockwell hardness can be improved by introducing metal salts (ionic crosslinks), and HDT and tensile and flexural strengths are also improved by selecting the most suitable concentration of metal salts according to the species of metal salts and vinyl monomers. On the other hand, impact strength generally has a tendency to decrease by introducing metal salts. Besides, the physical properties of the copolymers containing MMA are generally superior to those of the copolymers containing St.

Thermogravimetric Analysis

Figure 9 shows the TGA curves for the copolymer of $(EMP-)_2Zn$ (20 wt-%)-MMA-HEMA and the blank polymer (MMA-HEMA). The decomposition temperature was defined in the present study as the intersection of the two lines drawn on the curve before and after the major change in slope. The temperatures at 50% loss at which remarkable weight loss occurred were also determined. The copolymer of $(EMP-)_2Zn$ -MMA-HEMA and blank polymer showed decomposition temperatures of 255°C and 232°C, respectively, and temperatures of 340°C and 278°C, respectively, at 50% loss. That is, the copolymer containing Zn is thermally superior to one not containing Zn.

In the same way, from the TGA curves for the copolymer of $(EMP-)_2Zn$ (20 wt-%)-St-HEMA and blank polymer (St-HEMA) decomposition temperatures of 275°C for the former and 285°C for the latter, and temperatures at 50% loss of 334°C for the former and 345°C for the latter were obtained. In the copolymer containing St, introducing metal such as Zn has no effect on thermal stability. Moreover, it is known that both St-MAA

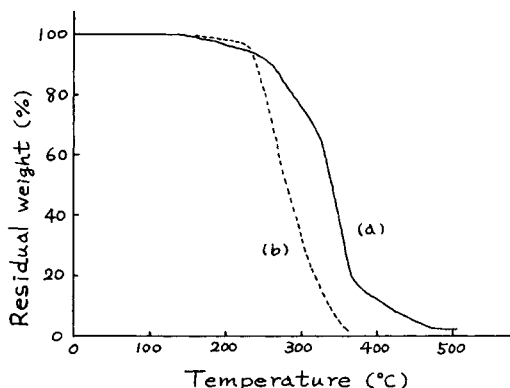


Fig. 9. TGA curve of copolymer obtained: (a) $(EMP-)_2Zn$ (20 wt-%)-MMA-HEMA; (b) blank polymer (MMA-HEMA).

copolymer and ionically crosslinked St-MAA copolymer as well as polystyrene begin to decompose above about 280°C.⁷ Generally, it seems that introducing metals into styrene polymers has no effect on thermal stability.

Boiling Water Resistance

The samples were immersed in boiling water for 30 hr. The change of state was observed visually.

In the copolymers of (EMP—)₂Cd-MMA, the surfaces of samples became a little semitransparent at low concentrations of (EMP—)₂Cd, white at high concentration of (EMP—)₂Cd, and eroded and rough at 40% (EMP—)₂Cd. Blank polymer (poly-MMA) showed no change. In the copolymers of (EMP—)₂Zn-MMA-HEMA and (EMP—)₂Zn or Cd-St-HEMA, the surfaces of all samples became white. Blank polymer (MMA-HEMA) showed no change, but in the blank polymer (St-HEMA) the surface became white. Generally, the copolymers containing St became white more markedly than those containing MMA did. No sample showed deformation.

On the other hand, in water at room temperature, all samples showed no change at all.

References

1. F. Ide and A. Hasegawa, *Kobunshi*, **18**, 616 (1969); F. Ide and A. Hasegawa, *Kobunshi*, **18**, 712 (1969).
2. B. A. Dolgoplas, E. I. Tinyakova, V. N. Rakh, and S. B. Petrova, *Rubber Chem. Technol.*, **32**, 321 (1959); H. P. Brown, *Rubber Chem. Technol.*, **30**, 1347 (1957).
3. R. W. Rees and D. J. Vaughan, *ACS Polymer Preprints*, **6**, 287, 296 (1965); S. Bonotto and C. L. Purcell, *Mod. Plast.*, 135, March (1965).
4. Ide and A. Hasegawa, *Kobunshi Kagaku*, **25**, 825 (1968).
5. *Kobunshi Jikkengaku Koza (Kyoritsu Shuppan)*, Vol. 9, p. 150.
6. F. Ide, T. Kodama, and A. Hasegawa, *Kobunshi Kagaku*, **27**, 58 (1970).
7. F. Ide, T. Kodama, A. Hasegawa, and O. Yamamoto, *Kobunshi Kagaku*, **26**, 873 (1969).

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