

## Preparation and Copolymerization of Divalent Metal Salts of Ethylene Glycol-Methacrylate-Maleate

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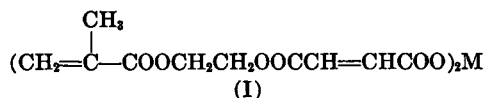
### Synopsis

Divalent metal salts of ethylene glycol-methacrylate-maleate (EMM) were prepared by the reaction of EMM and divalent metal ions. The divalent metal salts obtained, except for the Ba salt, have melting points which decrease in the order  $Pb > Ca > Cd > Mg > Zn$ . The Mg and Ca salts were selected for the copolymerization with MMA, styrene (St), and hydroxyethyl methacrylate. 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, heat distortion temperature, compressive strength, and Rockwell hardness were improved by introducing metal salts into the polymers, and tensile, flexural, and impact strengths are also able to be improved by selecting the most suitable concentration of metal salts according to the species of metal salts and vinyl monomers. Generally, Mg is more effective than Ca in improving the physical properties of the copolymers. Moreover, TGA and boiling water resistance of the copolymers are also discussed.

### INTRODUCTION

In the previous studies,<sup>1,2</sup> the polymerizable monomers containing an ionic bond were prepared by the metalation of ethylene glycol-methacrylate-phthalate (EMP) and were copolymerized with other vinyl monomers, and the chief properties of the copolymers obtained were discussed. From these investigations interesting results were obtained.

In the present study, divalent metal salts (I) of ethylene glycol-methacrylate-maleate (EMM) were prepared and were copolymerized with other vinyl monomers, and the chief properties of copolymers obtained were discussed:



where M = divalent metal (Mg, Ca, Zn, Cd, Ba, Pb).

The copolymers based on compound I are considered as forming network structures by both ionic bonds and covalent bonds.

EMM can be prepared easily by the addition reaction of commercially available hydroxyethyl methacrylate (HEMA) and maleic anhydride. Compounds I were prepared by the reaction of EMM with chlorides, oxides, and acetates of divalent metals. MMA, styrene (St), and HEMA were used as vinyl monomers.

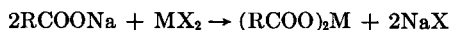
## EXPERIMENTAL

### Preparation of EMM

EMM was prepared by the addition reaction of HEMA and maleic anhydride. The method of preparation was as follows: Into a three-necked flask, 5622.9 g (43.2 moles) of HEMA, 3922.4 g (40 moles) of maleic anhydride and 130.8 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 (EMM) was 232.7 (calcd. 231.9). EMM was used without further purification.

### Preparation of Divalent Metal Salts (I) of EMM

#### *Method A*

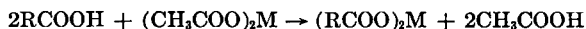


where Y = Cl, CH<sub>3</sub>COO.

**Preparation of Pb Salt (No. 11 in Table I).** Into a 45% aqueous solution of Na salt of EMM was added dropwise a 35% aqueous solution of an equivalent amount of (CH<sub>3</sub>COO)<sub>2</sub>Pb·3H<sub>2</sub>O with stirring at room temperature. As the reaction proceeded, produced Pb salt precipitated in the form of white precipitate. After reaction, the product was washed with distilled water and dried in vacuo at room temperature.

**Preparation of Ca Salt (No. 3 in Table I).** Into a 40% methanol solution of Na salt of EMM was added dropwise a 10% *m*-ethanol solution of equivalent amount of CaCl<sub>2</sub>·2H<sub>2</sub>O with stirring at 40°C over 30 min. After addition, the stirring was continued for additional 10 min, and then the mixture was filtered to remove NaCl (by-product). The methanol was removed by distillation under reduced pressure from the filtrate, to obtain a viscous liquid. The viscous liquid was dissolved in acetone, and, after filtration, the solution was added into ether to yield the product.

#### *Method B*



### Preparation of Pb Salt (No. 12 in Table I)

Into a three-necked flask in which EMM was dispersed in a large amount of water with stirring, an aqueous solution of an equivalent amount of (CH<sub>3</sub>COO)<sub>2</sub>Pb·3H<sub>2</sub>O was added dropwise at room temperature over 30 min. After addition, the stirring was continued for an additional 30 min, and

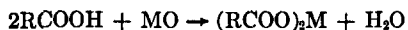
TABLE I  
Synthesized Metal Salts of EMM

| Metal | Expt. no. | Method of synthesis | Solvent  | Yield, % | Melting point, °C | Metal, % |        | Bromine no. |        |
|-------|-----------|---------------------|--|----------|-------------------|----------|--------|-------------|--------|
|       |           |                     |  |          |                   | Found    | Calcd. | Found       | Calcd. |
| Mg    | 1         | C                   | C <sub>6</sub> H <sub>6</sub> *                  | 78       | 41-45             | 5.12     | 5.08   | 64          | 67     |
|       | 2         | C                   | H <sub>2</sub> O                                 | 60       | 42-47             | 4.91     |        | 57          |        |
| Ca    | 3         | A                   | CH <sub>3</sub> OH                               | 33       |                   | 12.59    | 8.11   |             | 65     |
|       | 4         | C                   | C <sub>6</sub> H <sub>6</sub>                    | 75       | 64-67             | 7.87     |        | 63          |        |
| Zn    | 5         | C                   | C <sub>6</sub> H <sub>6</sub>                    | 38       |                   | 15.90    | 12.58  |             | 62     |
|       | 6         | C                   | H <sub>2</sub> O                                 | 71       | 27-29             | 12.41    |        | 57          |        |
| Cd    | 7         | C                   | C <sub>6</sub> H <sub>6</sub>                    | 80       | 50-52             | 19.30    | 19.83  | 52          | 56     |
|       | 8         | C                   | CH <sub>3</sub> COOC <sub>2</sub> H <sub>5</sub> | 78       | 50-51             | 19.78    |        | 52          |        |
| Ba    | 9         | C                   | CHCl <sub>3</sub>                                | 77       | —                 | 22.90    | 23.21  | 53          | 54     |
|       | 10        | C                   | C <sub>6</sub> H <sub>6</sub>                    | 55       | —                 | 22.79    |        | 51          |        |
| Pb    | 11        | A                   | H <sub>2</sub> O                                 | 29       |                   | 35.98    | 31.31  |             | 48     |
|       | 12        | B                   | H <sub>2</sub> O                                 | 58       | 110-115           | 31.58    |        | 47          |        |
|       | 13        | C                   | C <sub>6</sub> H <sub>6</sub>                    | 88       | 115-118           | 31.27    |        | 45          |        |

\* Contained a small quantity of water.

then the precipitated product was separated and dried in vacuo at room temperature.

#### *Method C*



Into a three-necked flask in which EMM dissolved in a solvent was placed was added an equivalent amount of oxide of divalent metal with stirring at room temperature. After addition, the stirring was continued at room temperature (65°C) for 1 to 3 hr. After reaction, the mixture was filtered. Upon standing, the product separated as white crystals from the filtrate, and was washed with ether and dried in vacuo at room temperature.

The bromine numbers of the products were determined according to the bromination method.<sup>3</sup>

#### **Copolymerization of Metal Salts I and Vinyl Monomers**

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

The method of preparation of resin boards for determining physical properties was as follows: To a 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 degasification, polymerized at a fixed temperature for a fixed time.

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

#### **Determination of Physical Properties**

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

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

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

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

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 thermobalance TGA-20 of Shimadzu Seisakusho at a heating rate of 5°C/min in air.

## RESULTS AND DISCUSSION

### Preparation of Metal Salts I

The results of preparation of metal salts I are summarized in Table I.

The bromine numbers were determined on the products whose metal contents agreed well with calculated values. I can be prepared generally by method C with good results.

In case of the Mg salt, when the synthetic reaction was carried out by method C in benzene containing a small quantity of water, good results could be obtained. When the synthetic reaction was carried out by method C in aqueous solution, the product precipitated as white crystals from the solution upon standing after addition of the seed crystal. The bromine number of the product thus obtained, however, was lower than the calculated value.

In case of the Ca salt, when the synthetic reaction was carried out by method A in methanol, the yield was low and the metal content of the product was higher than the calculated value. On the other hand, when the synthetic reaction was carried out by method C in benzene, good result could be obtained. However, when water was used as solvent in this case, the product did not separate from the solution.

In case of the Zn salt, when the synthetic reaction was carried out by method C in benzene, the yield was low and the metal content of the product was higher than the calculated value. On the other hand, when water was used as solvent, the product separated as white crystals from the solution upon standing after addition of the seed crystal. The metal content of the product thus obtained agreed well with the calculated value and the yield was high.

In case of the Cd and Ba salts, when the synthetic reaction was carried out by method C in organic solvents such as benzene, ethyl acetate, or chloroform, good results could be obtained.

In case of the Pb salt, when the synthetic reaction was carried out by method B in aqueous solution and by method C in benzene, good results could be obtained.

The metal salts obtained, except for the Ba salt, have melting points which decrease in the order  $Pb > Ca > Cd > Mg > Zn$ . In the infrared spectra of the metal salts obtained, an absorption band in the region of  $1560-1600\text{ cm}^{-1}$ , which is characteristic of carboxylate (antisymmetric stretching vibration) and cannot be seen in case of EMM, is observed. This means that a static ionic bond between  $-\text{COO}^-$  and  $M^{++}$  is formed. Moreover, absorption bands about  $1630$  and  $940\text{ cm}^{-1}$ , which are characteristic of the terminal vinyl group, are observed.

The solubility characteristics of the metal salts of high purity are shown in Table II. Mg salt, Ca salt, and Cd salt show good solubility in chief organic solvents. In ethyl ether, however, all of the metal salts are insoluble. Among the above metal salts, the Mg and Ca salts were selected

TABLE II  
Solubility of Metal Salts of EMM<sup>a</sup>

| 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         | +       | +       | +       | +       | +—      | —       |

<sup>a</sup> (+) Soluble, (+—) partially soluble, (—) insoluble.

as the monomers suitable for preparing copolymers, judging from solubility and industrial advantageousness.

Next, the copolymerization of the Mg and Ca salts, with MMA, St, and HEMA was carried out. The Mg and Ca salts which were used in the copolymerization were prepared according to the method of no. 1 (method C) and no. 4 (method C) in Table I, respectively.

### Copolymerization

The solubilities of (EMM-)<sub>2</sub>Mg and (EMM-)<sub>2</sub>Ca in St are as shown in Table II; however, these metal salts are soluble in the mixture of St and HEMA. In MMA, these metal salts are soluble, whereas the metal salt-MMA systems, when polymerized, showed a tendency to become heterogeneous. Such a tendency was not observed in the metal salt-MMA-HEMA systems. As a result of preliminary experiments, it was found that the St or MMA/HEMA ratio suitable for obtaining satisfactory compositions for copolymerization is 2.5/1 (by weight). Therefore, in the mixtures of this constant ratio the metal salts were dissolved in various quantities and the compositions were copolymerized.

The time-conversion curves for the copolymerization are shown in Figures 1 and 2. In all systems, the rates of polymerization increased markedly as the concentration of metal salts increased. (This tendency is a phenomenon characteristic of the polyvinyl compounds, namely, it is considered that, as the concentration of metal salts which are polyvinyl compounds increases, the viscosity of polymerization system increases so that the rate of polymerization increases by means of the so-called "gel effect.") The same tendency was observed in the previous study.<sup>1</sup> Besides, the rates of polymerization of the systems containing MMA are much higher than those of the systems containing St and, at 45°C conversion, reached nearly the maximum conversion attainable after about 5–8 hr. In the systems containing St, when the concentration of metal

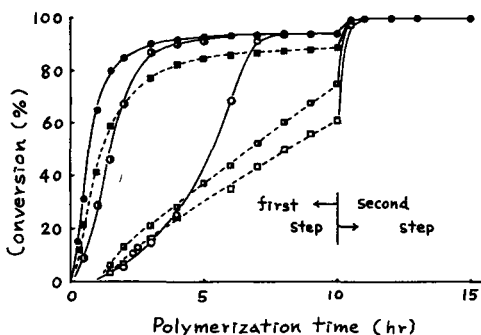


Fig. 1. Time-conversion curves for copolymerization of  $(\text{EMM})_2\text{Mg}$ -vinyl monomers: (○)  $(\text{EMM})_2\text{Mg}$  5 wt-%, MMA-HEMA (2.5/1) 95 wt-%; (◐)  $(\text{EMM})_2\text{Mg}$  10 wt-%, MMA-HEMA 90 wt-%; (◑)  $(\text{EMM})_2\text{Mg}$  30 wt-%, MMA-HEMA 70 wt-%; (□)  $(\text{EMM})_2\text{Mg}$  5 wt-%, St-HEMA (2.5/1) 95 wt-%; (◒)  $(\text{EMM})_2\text{Mg}$  10 wt-%, St-HEMA 90 wt-%; (◓)  $(\text{EMM})_2\text{Mg}$  30 wt-%, St-HEMA 70 wt-%.

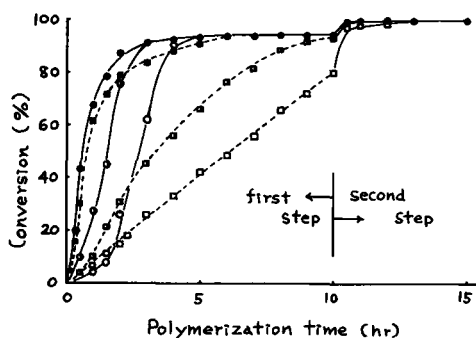


Fig. 2. Time-conversion curves for copolymerization of  $(\text{EMM})_2\text{Ca}$ -vinyl monomers: (○)  $(\text{EMM})_2\text{Ca}$  5 wt-%, MMA-HEMA (2.5/1) 95 wt-%; (◐)  $(\text{EMM})_2\text{Ca}$  10 wt-%, MMA-HEMA 90 wt-%; (◑)  $(\text{EMM})_2\text{Ca}$  30 wt-%, MMA-HEMA 70 wt-%; (□)  $(\text{EMM})_2\text{Ca}$  5 wt-%, St-HEMA (2.5/1) 95 wt-%; (◒)  $(\text{EMM})_2\text{Ca}$  10 wt-%, St-HEMA 90 wt-%; (◓)  $(\text{EMM})_2\text{Ca}$  30 wt-%, St-HEMA 70 wt-%.

salts is low, conversion did not reach the maximum conversion attainable even after 10 hr. Successively, the second-step polymerizations were carried out at  $100^\circ\text{C}$ ; as a result, it was found that the conversion of all systems reached the maximum conversion attainable within 1 hr.

In all cases, the observed gelation of the polymerization systems occurred at 8–20% conversion. Moreover, at the beginning of polymerization, the copolymers obtained contained a large quantity of chloroform-soluble part, but as the conversion increased, the chloroform-soluble part decreased markedly and became negligible above 25% conversion.

The copolymers obtained were generally transparent; however, those containing a large quantity of  $(\text{EMM})_2\text{Ca}$  were slightly semitransparent.

According to the results of the copolymerization mentioned above, the polymerization condition for obtaining samples for determining physical properties was set up as follows: first-step polymerization at  $35\text{--}45^\circ\text{C}$

for 15 hr, second-step polymerization at 100°C for 5 hr, further, third-step polymerization at 110°C for 1 hr.

### Physical Properties of Copolymers

The concentration of metal salts in the copolymers used for determining physical properties was up to about 30 wt-%. The weight ratio of MMA or St and HEMA was 2.5:1.

**HDT.** As shown in Figure 3, in the copolymers containing MMA, above 10% metal salts HDT increases gradually with increase in metal salts. The influence of the species of metals is not observed in this case. In the copolymers containing St, HDT increases markedly with increase in the metal salts, and, besides, Mg is more effective than Ca in this case. For instance, at 30% metal salts, an approximate 20°C increase in HDT is observed in case of Mg, whereas an approximate 11°C increase is seen in case of Ca.

**Tensile Strength.** As is clear from Figure 4, in the (EMM-)<sub>2</sub>Mg-MMA-HEMA copolymers, tensile strength reaches a peak at 5% (EMM-)<sub>2</sub>Mg; further increase in (EMM-)<sub>2</sub>Mg reduces the tensile strength markedly. In the (EMM-)<sub>2</sub>Ca-MMA-HEMA copolymers, tensile strength decreases markedly with increase in (EMM-)<sub>2</sub>Ca. Generally, the tensile strength of the former copolymers is superior to that of the latter copolymers. In the copolymers containing St, tensile strength has a peak at 5% metal salts, at which an increase of about 180 kg/cm<sup>2</sup> in case of Mg and 140 kg/cm<sup>2</sup> in case of Ca is observed. Further increase in the metal salts reduces the tensile strength. 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,<sup>4</sup> and that in the glassy

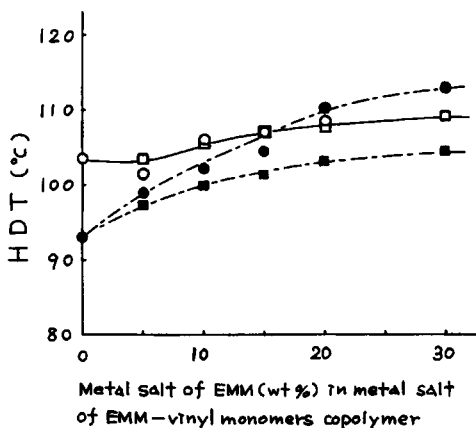


Fig. 3. Effect of metal salt of EMM on HDT of metal salt of EMM-vinyl monomers copolymer: (O) (EMM-)<sub>2</sub>Mg-MMA-HEMA; (●) (EMM-)<sub>2</sub>Mg-St-HEMA; (□) (EMM-)<sub>2</sub>Ca-MMA-HEMA; (■) (EMM-)<sub>2</sub>Ca-St-HEMA. Weight ratio of MMA or St/HEMA = 2.5/1.



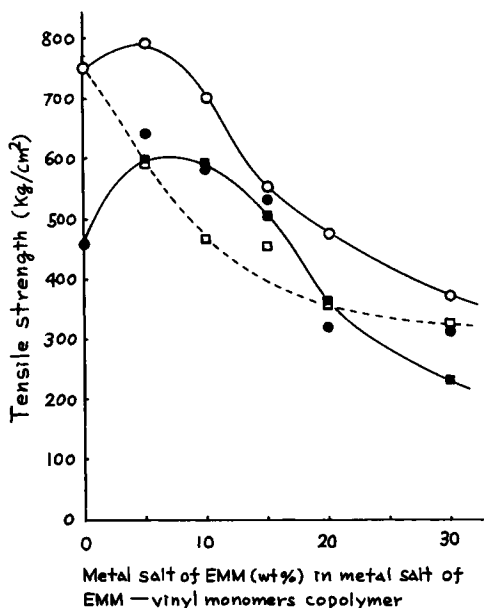


Fig. 4. Effect of metal salt of EMM on tensile strength of metal salt of EMM-vinyl monomers copolymer: (O) (EMM-)₂Mg-MMA-HEMA; (●) (EMM-)₂Mg-St-HEMA; (□) (EMM-)₂Ca-MMA-HEMA; (■) (EMM-)₂Ca-St-HEMA. Weight ratio of MMA or St/HEMA = 2.5/1.

St-methacrylic acid (MAA)-ethyl acrylate (EA) copolymer, tensile strength rather decreased as the degree of ionic crosslinking increased.<sup>5</sup> Furthermore, it is known that also in the glycol dimethacrylate-MMA or St. copolymers which are crosslinked by covalent bonds, increase in glycol dimethacrylate rather reduces tensile strength.<sup>6</sup>

**Flexural Strength.** As shown in Figure 5, in the copolymers of (EMM-)₂Mg-MMA-HEMA flexural strength has a peak at 5% (EMM-)₂Mg, at which an increase of about 130 kg/cm<sup>2</sup> is observed. In the copolymers of (EMM-)₂Ca-HEMA, flexural strength remains nearly unchanged up to about 10% (EMM-)₂Ca, above which it decreases markedly with increase in (EMM-)₂Ca. On the other hand, in the copolymers containing St, flexural strength increases markedly with increase in the metal salts, and Mg is more effective than Ca in this case. For instance, at 15% metal salts, a 425 kg/cm<sup>2</sup> increase in flexural strength is observed in case of Mg, where a 310 kg/cm<sup>2</sup> increase is observed in case of Ca. In this case, the effect of introducing the metal salts appears marked.

**Compressive Strength.** As is clear from Figure 6, in all copolymers compressive strength increases markedly with increase in the metal salts. For instance, at 30% metal salts, a 350-380 kg/cm<sup>2</sup> increase in compressive strength is observed in the copolymers containing MMA, and an approximate 270 kg/cm<sup>2</sup> increase in those containing St. Moreover, in the copolymers containing St, Mg is more effective than Ca below about 20%

metals salts. Thus, in compressive strength the effect of introducing metal salts appears marked.

**Impact Strength.** As shown in Figure 7, in the copolymers containing MMA impact strength decreases with increase in the metal salts. Gen-

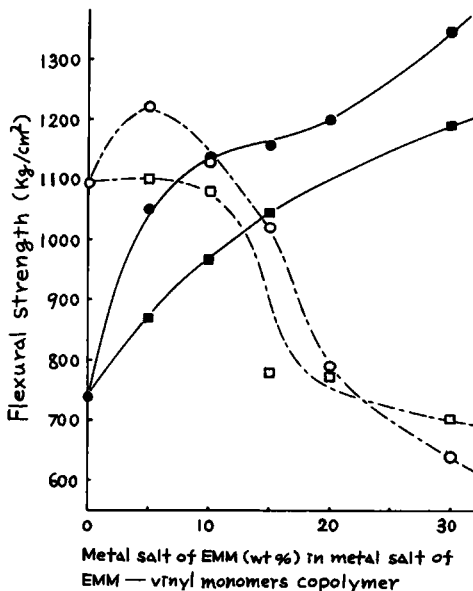


Fig. 5. Effect of metal salt of EMM on flexural strength of metal salt of EMM-vinyl monomers copolymer: (O) (EMM)<sub>2</sub>Mg-MMA-HEMA; (●) (EMM)<sub>2</sub>Mg-St-HEMA; (□) (EMM)<sub>2</sub>Ca-MMA-HEMA; (■) (EMM)<sub>2</sub>Ca-St-HEMA. Weight ratio of MMA or St/HEMA = 2.5/1.

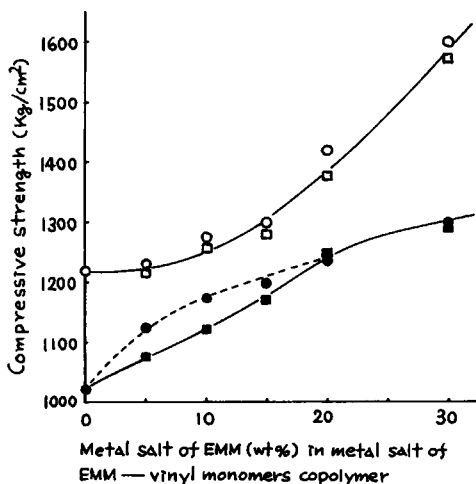


Fig. 6. Effect of metal salt of EMM on compressive strength of metal salt of EMM-vinyl monomers copolymer: (O) (EMM)<sub>2</sub>Mg-MMA-HEMA; (●) (EMM)<sub>2</sub>Mg-St-HEMA; (□) (EMM)<sub>2</sub>Ca-MMA-HEMA; (■) (EMM)<sub>2</sub>Ca-St-HEMA. Weight ratio of MMA or St/HEMA = 2.5/1.

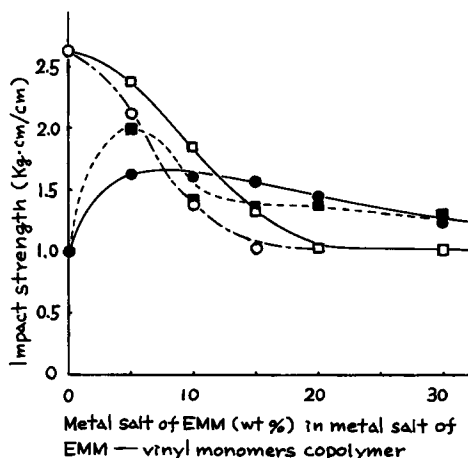


Fig. 7. Effect of metal salt of EMM on impact strength of metal salt of EMM-vinyl monomers copolymer: (O) (EMM-)<sub>2</sub>Mg-MMA-HEMA; (●) (EMM-)<sub>2</sub>Mg-St-HEMA; (□) (EMM-)<sub>2</sub>Ca-MMA-HEMA; (■) (EMM-)<sub>2</sub>Ca-St-HEMA. Weight ratio of MMA or St/HEMA = 2.5/1.

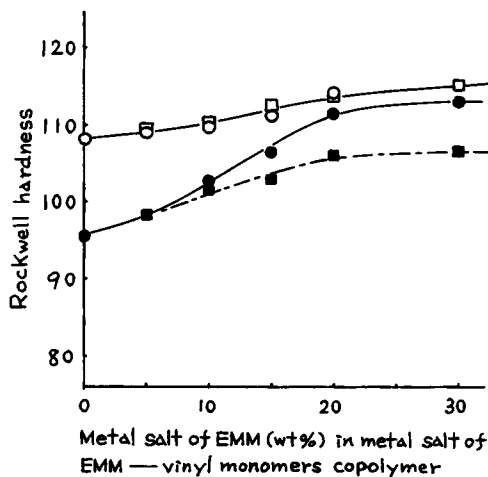


Fig. 8. Effect of metal salt of EMM on Rockwell hardness of metal salt of EMM-vinyl monomers copolymer: (O) (EMM-)<sub>2</sub>Mg-MMA-HEMA; (●) (EMM-)<sub>2</sub>Mg-St-HEMA; (□) (EMM-)<sub>2</sub>Ca-MMA-HEMA; (■) (EMM-)<sub>2</sub>Ca-St-HEMA. Weight ratio of MMA or St/HEMA = 2.5/1.

erally, the impact strength of the (EMM-)<sub>2</sub>Ca-MMA-HEMA copolymers is superior to that of the (EMM-)<sub>2</sub>Mg-MMA-HEMA copolymers. On the other hand, in the copolymers containing St, impact strength is improved by introducing the metal salts, and in the (EMM-)<sub>2</sub>Ca-St-HEMA copolymers, impact strength has a peak of 2.0 at 5% (EMM-)<sub>2</sub>Ca. Similarly, in the Cr salt of EMP-St copolymers in the previous study, impact strength has a peak at 5% Cr salt.<sup>2</sup>

**Rockwell Hardness.** As is clear from Figure 8, in all copolymers Rockwell hardness increases as the metal salts increase. In the copolymers

containing MMA, the influence of the species of metals is not observed. On the other hand, in the copolymers containing St, Mg is more effective than Ca in improving Rockwell hardness. In Rockwell hardness, too, the effect of introducing metal salts appears marked.

As summary of the results described above, the following may be concluded: HDT, compressive strength, and Rockwell hardness can be improved by introducing metal salts, and tensile, flexural, and impact strengths are also able to be improved by selecting the most suitable concentration of metal salts according to the species of metal salts and vinyl monomers. Generally, Mg is more effective than Ca in improving the physical properties of the copolymers on the present study. This is considered to be due to the fact that the interionic attraction of  $Mg^{++}$  is larger than that of  $Ca^{++}$ .

### TGA

Figure 9 shows the TGA curves for the copolymers containing MMA. The decomposition temperature was defined, in the same way as described in the previous report,<sup>1</sup> 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 copolymers of  $(EMM-)_2Mg$ -MMA-HEMA and  $(EMM-)_2Ca$ -MMA-HEMA showed decomposition temperatures of 265°C and 270°C, respectively, and temperatures at 50% loss of 326°C and 330°C, respectively. On the other hand, the blank polymer showed a decomposition temperature of 232°C, and a temperature at 50% loss of 267°C. That is, the copolymers containing metal are thermally superior to those not containing metal. A similar tendency was observed in the copolymer of the Zn salt of EMP-MMA-HEMA in the previous study.<sup>1</sup>

In the same way, from TGA curves for the copolymers of  $(EMM-)_2Mg$  (20 wt-%)-St-HEMA and  $(EMM-)_2Ca$  (20 wt-%)-St-HEMA, and blank

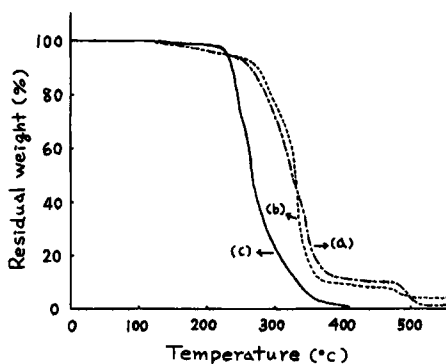


Fig. 9. TGA curves of copolymers obtained: (a)  $(EMM-)_2Mg$  (20 wt-%)-MMA-HEMA; (b)  $(EMM-)_2Ca$  (20 wt-%)-MMA-HEMA; (c) blank polymer (MMA-HEMA).

polymer (St-HEMA), the respective decomposition temperatures of 283°C, 285°C, and 287°C, and at 50% loss of 325°C, 330°C, and 337°C were obtained.

In the copolymers containing St, introducing metal such as Mg and Ca shows no effect on thermal stability. Moreover, it is known that both St-MAA copolymer and ionically crosslinked St-MAA copolymer as well as polystyrene begin to decompose above about 280°C<sup>4</sup> Generally, it seems that introducing metals into styrene polymers shows 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 (EMM-)<sub>2</sub>Mg-MMA-HEMA and (EMM-)<sub>2</sub>Ca-MMA-HEMA, the surfaces of samples became white, and at high concentration of metal salts the surfaces were considerably eroded and became rough. Blank polymer (MMA-HEMA) showed no change. In the copolymers of (EMM-)<sub>2</sub>Mg-St-HEMA, the surfaces of samples became slightly semitransparent at low concentration of (EMM-)<sub>2</sub>Mg, white at high concentration of (EMM-)<sub>2</sub>Mg, and at 30% (EMM-)<sub>2</sub>Mg the surface was considerably eroded. In the copolymers of (EMM-)<sub>2</sub>Ca-St-HEMA, the surfaces of all samples became white, and at 30% (EMM-)<sub>2</sub>Ca the surface was considerably eroded. In the blank polymer (St-HEMA), the surface became white.

Generally, the copolymers containing Ca became white more markedly than those containing Mg did. On the other hand, in water at room temperature, all copolymers showed no change at all, except for the 30% (EMM-)<sub>2</sub>Ca-containing copolymer of (EMM-)<sub>2</sub>Ca-MMA-HEMA, the surface of which became slightly semitransparent.

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