

Preparation and Copolymerization of Polyvalent Metal Salts of Ethyleneglycol-methacrylate-maleate

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Synopsis

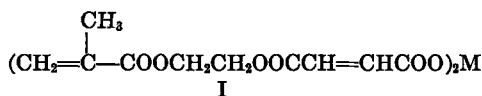
Preparation of polyvalent metal salts of ethyleneglycol-methacrylate-maleate (EMM) was investigated by the reaction of Na salt of EMM and chlorides of polyvalent metals such as Al^{3+} , Cr^{3+} , Fe^{3+} , Ni^{2+} , Co^{2+} , and Cu^{2+} . It was found that, among the metal salts obtained, the Cr salt could be obtained in the form of $(EMM-)_2Cr(OH)$ in high purity, where EMM— means EMM residue,



Then, $(EMM-)_2Cr(OH)$ was copolymerized with styrene, MMA, and hydroxyethyl methacrylate. In the copolymerization, the rates of copolymerization increased markedly as the concentration of $(EMM-)_2Cr(OH)$ increased. As for the physical properties of the copolymers obtained, Rockwell hardness and compressive strength can be improved by introducing $(EMM-)_2Cr(OH)$ into the polymers, and HDT, tensile, and flexural strengths can also be improved by selecting the most suitable concentration of $(EMM-)_2Cr(OH)$ according to the species of vinyl monomer. Further, TGA and boiling water resistance of the copolymers are also discussed.

INTRODUCTION

In the previous study,¹ divalent metal salts (I) of ethyleneglycol-methacrylate-maleate (EMM) were prepared as the polymerizable monomers containing an ionic bond, and I were copolymerized with other vinyl monomers, and the chief properties of the copolymers obtained were discussed. From this investigation, interesting results were obtained. The copolymers based on I are considered as forming network structures by both ionic bonds and covalent bonds:



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

On the other hand, previously we investigated the metalation of ethyleneglycol-methacrylate-phthalate (EMP) by such polyvalent metals as Al^{3+} , Cr^{3+} , Fe^{3+} , Ni^{2+} , Co^{2+} , and Cu^{2+} and found that the Cr salt could be obtained in high purity.² In the present study, we investigated metalation of EMM by these polyvalent metals and found that, also in this case, the Cr salt could be obtained in high purity. So, the Cr salt obtained was copoly-

merized with other vinyl monomers and the chief properties of copolymers obtained were discussed.

EMM can be prepared easily by the addition reaction of commercially available hydroxyethyl methacrylate (HEMA) and maleic anhydride. By the reaction of the Na salt of EMM and chlorides of polyvalent metals, the preparation of polyvalent metal salts of EMM was investigated. MMA, styrene (St), and HEMA were used as vinyl monomers.

Meanwhile, the patent literature³ mentions the curable compositions consisting of polymerizable monomers and metal-containing compounds which are the reaction products of EMM and alcoholates of polyvalent metals such as Al, Ti, V, Sb, Cr, Co, and Ni. But details on metal-containing compounds and the properties of cured materials obtained therefrom have not been published.

EXPERIMENTAL

EMM was prepared by the addition reaction of HEMA and maleic anhydride, according to the method reported in the previous paper¹; the acid value was 232.6 (calcd 231.9). EMM was used without further purification.

Preparation of Polyvalent Metal Salts of EMM

To a three-necked flask in which 100 g EMM had been placed was added dropwise a solution of an equivalent amount of Na_2CO_3 dissolved in 100 g water with stirring at room temperature, to obtain the Na salt.

To the aqueous solution of the Na salt of EMM prepared above was added dropwise a solution of a fixed amount of metal chloride ($\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$) dissolved in 100 g water with stirring at room temperature. After the addition, the stirring was continued for 1 hr, and then 300 g chloroform was added to the mixture with stirring to extract the product. After the separation of the organic and the aqueous layers, to the organic layer (the extracted mixture) was added 150–300 g 8% aqueous solution of NaHCO_3 for neutralization. (When the insoluble substance was formed, it was removed by filtration.) After neutralization, the organic layer was separated and washed with water several times to remove an excess of alkali. (When the insoluble substance was formed in this case, it was again removed by filtration.)

The organic layer thus obtained was treated by the following methods to obtain the product: (A) the chloroform was removed by distillation under reduced pressure from the organic layer to yield the product, (B) the product obtained in A was dissolved in acetone, and then the solution was added dropwise to a great quantity of vigorously stirred water, precipitating the product. The product was dried *in vacuo* at room temperature. This procedure was repeated several times according to circumstances.

The symbols A and B in Table I refer to the method of treatment mentioned above. When the reaction was carried out in methanol, the pro-

TABLE I
 Synthesized Metal Salts of EMM

Metal	Expt. no.	Mole ratio of reactants	Method of treatment	Yield, ^a g	External appearance	Metal, %	
						Found	Calcd
Al	1	EMM/AlCl ₃ ·6H ₂ O = 2	A	36	slightly yellow, glassy material	7.99	9.36 for (EMM—) ₂ Al(OH) ₂ 5.42 for (EMM—) ₂ Al(OH)
	2	EMM/AlCl ₃ ·6H ₂ O = 2	B	22	white powder	9.86	3.81 for (EMM—) ₂ Al
Cr	3	EMM/AlCl ₃ ·6H ₂ O = 2	B ^b	56	white powder	9.50	(EMM—) ₂ Cr(OH)
	4	EMM/CrCl ₃ ·6H ₂ O = 3	B	50	deep-blue powder	10.22	16.60 for (EMM—) ₂ Cr(OH) ₂ 9.94 for (EMM—) ₂ Cr(OH)
Fe	5	EMM/CrCl ₃ ·6H ₂ O = 2	A	74	deep-blue, glassy material	9.14	(EMM—) ₂ Cr(OH)
	6	EMM/CrCl ₃ ·6H ₂ O = 2	B	52	deep-blue powder	9.80	(EMM—) ₂ Cr(OH)
Fe	7	EMM/FeCl ₃ ·6H ₂ O = 3	B	27	brown powder	21.15	17.61 for (EMM—) ₂ Cr
	8	EMM/FeCl ₃ ·6H ₂ O = 2	A	43	brown viscous material	16.93	(EMM—) ₂ Fe(OH) ₂ 10.59 for (EMM—) ₂ Fe(OH)
Ni	9	EMM/FeCl ₃ ·6H ₂ O = 2	B	34	brown powder	20.04	7.57 for (EMM—) ₂ Fe
	10	EMM/NiCl ₂ ·6H ₂ O = 2	A	34	green, glassy material	14.54	19.38 for (EMM—) ₂ Ni(OH)
Co	11	EMM/NiCl ₂ ·6H ₂ O = 2	B	20	slightly green powder	24.47	11.44 for (EMM—) ₂ Ni
	12	EMM/CoCl ₂ ·6H ₂ O = 2	c	82	cobalt blue, glassy material	12.34	19.44 for (EMM—) ₂ Co(OH)
Cu	13	EMM/CuCl ₂ ·2H ₂ O = 2	d	56	blue-green powder	12.19	11.48 for (EMM—) ₂ Co 20.65 for (EMM—) ₂ Cu(OH) 12.27 for (EMM—) ₂ Cu

^a EMM was used at amount of 100 g.

^b Synthesized in methanol.

^c The product separated as crystals during the synthetic reaction. For purification, the crystals were dissolved in acetone and, after filtration, the acetone was removed from the filtrate to yield the product.

^d Precipitated from chloroform to ethyl ether-petroleum ether (2/1) without alkali treatment.

cedure was based on the method mentioned above. However, in this case, to the methanol solution of the Na salt of EMM was added dropwise a fixed amount of metal chloride dissolved in methanol with stirring at room temperature, and then the stirring was continued for 2 hr. After the reaction, the methanol was removed by distillation under reduced pressure, and then the product was dissolved in chloroform. Thereafter, the solution was treated in the same way as mentioned above.

The bromine numbers of the products were determined according to the bromination method.⁴

Copolymerization of Cr Salt with Vinyl Monomers

The Ampoule polymerization for determining the conversion in the copolymerization of Cr salt 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 the mixture of Cr salt 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.

MMA and St of chemically 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 638-64 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 thermobalance TGA-20 of Shimazu Seisakusho at a heating rate of 5°C/min in air.

RESULTS AND DISCUSSION

Preparation of Polyvalent Metal Salts of EMM

In Table I are summarized the results of the preparation of polyvalent metal salts of EMM. "Yield" is expressed by "gram" (weight) of the

product obtained from 100 g EMM. Hereafter, EMM residue will be denoted by EMM—.

The preparation of polyvalent metal salts of EMM in the present study was investigated, in the same way as described in the previous report,² by the reaction of Na salt of EMM and chlorides of polyvalent metals. The reaction proceeded generally in aqueous solution. After the synthetic reaction, chloroform was added to the mixture to extract the product. When the organic layer was treated with aqueous solution of NaHCO_3 , carbon dioxide evolved. The organic layer washed with water after alkali treatment is considered to consist of chloroform and the products. The products could be obtained by treating the organic layer according to method A or B mentioned above.

In case of the Al salt, the product obtained by method A is considered to be a mixture of $(\text{EMM—})\text{Al}(\text{OH})_2$ and $(\text{EMM—})_2\text{Al}(\text{OH})$, judging from the found value of the metal content. On the other hand, the found values of metal content of the products obtained by method B agreed well with the calculated value for $(\text{EMM—})\text{Al}(\text{OH})_2$, regardless of the solvent during synthetic reaction.

In case of the Cr salt, the found values of metal content of the products obtained by method B agreed well with the calculated value for $(\text{EMM—})_2\text{Cr}(\text{OH})$, regardless of the mole ratios of reactants. Similarly, the found value of metal content of the product obtained by method A agreed considerably well with the calculated value for $(\text{EMM—})_2\text{Cr}(\text{OH})$.

In case of the Fe salt, the found value of metal content of the product obtained by method A agreed considerably well with the calculated value for $(\text{EMM—})\text{Fe}(\text{OH})_2$. On the other hand, the products obtained by method B are considered to be a mixture of $(\text{EMM—})\text{Fe}(\text{OH})_2$ and $\text{Fe}(\text{OH})_3$, judging from the found values of metal content. It is considered that part of $(\text{EMM—})\text{Fe}(\text{OH})_2$ was hydrolyzed to EMM and $\text{Fe}(\text{OH})_3$ during treatment by method B.

In case of the Ni salt, the product obtained by method A is considered to be a mixture of $(\text{EMM—})\text{Ni}(\text{OH})$ and $(\text{EMM—})_2\text{Ni}$, judging from the found value of metal content. On the other hand, the product obtained by method B is considered to be a mixture of $(\text{EMM—})_2\text{Ni}(\text{OH})$ and $\text{Ni}(\text{OH})_2$.

In case of the Co salt, the product separated as crystals during the synthetic reaction. The crystals were insoluble in chloroform. For purification, the crystals were dissolved in acetone and, after filtration, the acetone was removed by distillation under reduced pressure from the filtrate, to yield the product. The found value of metal content of the product thus obtained was relatively closer to the calculated value for $(\text{EMM—})_2\text{Co}$, and the yield was high. However, this Co salt was unstable to water and readily hydrolyzed.

In case of the Cu salt, the product was purified by precipitation from chloroform to ethyl ether-petroleum ether (2/1) without alkali treatment. The found value of the metal content of the product thus obtained agreed well with the calculated value for $(\text{EMM—})_2\text{Cu}$.

TABLE II
 Analysis of Synthesized Cr and Cu Salts of EMM

Metal salt	Calcd for	C, %	H, %	M, % ^a	Bromine no.
Cr salt (no. 6)	(EMM—)Cr(OH) ₂	45.98	4.75	9.80	60
	(EMM—) ₂ Cr(OH)	38.35	4.18	16.60	51
	(EMM—) ₂ Cr(OH)	45.89	4.43	9.94	61
	(EMM—) ₂ Cr	49.12	4.53	7.09	65
Cu salt (no. 13)	(EMM—) ₂ Cr	44.38	4.87	12.19	51
	(EMM—)Cu(OH)	39.02	3.94	20.65	52
	(EMM—) ₂ Cu	46.37	4.29	12.27	61

^a M = Metal.

The products obtained by method A were glassy or viscous materials, and those obtained by method B were powders. The Fe, Ni, and Co salts of EMM were less stable to water than those of EMP in the previous study.² Among the metal salts obtained, the Cr salt and the Cu salt were considered to contain two EMM residues per molecule.

The Cr salt (no. 6) and the Cu salt (no. 13) were then further analyzed, and the analytical data are shown in Table II. In case of the Cr salt, the found values of the elemental analysis and the bromine number agreed well with the calculated values for (EMM—)₂Cr(OH). In case of the Cu salt, the found bromine number was considerably lower than the calculated value for (EMM—)₂Cu. This tendency was observed also in the case of the Cu salt of EMP.² Moreover, in the infrared spectrum of the Cr salt, an absorption band about 1540 cm⁻¹, which is characteristic of carboxylate and cannot be seen in case of EMM, is observed and, besides, absorption bands about 1630 and 940 cm⁻¹, which are characteristic of the terminal vinyl group, are observed.

The Cr salt obtained is soluble in chief organic solvents such as benzene, acetone, chloroform, dioxane, ethyl acetate, tetrahydrofuran, and HEMA, and insoluble in methanol, ethanol, ethyl ether, *n*-hexane, and water.

As a summary of the results described above, it was found that, among the above metal salts, the Cr salt can be obtained in the form of (EMM—)₂Cr(OH) in high purity.

Therefore, copolymerization of the Cr salt with St, MMA, and HEMA was carried out. The Cr salt used in the copolymerization was prepared according to the method of experiment no. 6 in Table I. The Cr salt will be denoted hereafter by (EMM—)₂Cr(OH).

Copolymerization

The (EMM—)₂Cr(OH) is partially soluble in St and MMA; 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 St or MMA and HEMA in the ratio of 10:1 (weight) dissolves (EMM—)₂Cr(OH) up to about 15 wt-%. Therefore, in mixtures of

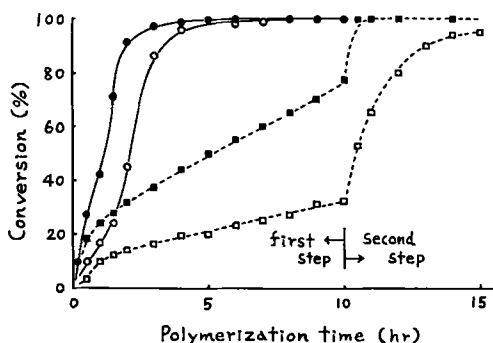


Fig. 1. Time-conversion curves for the copolymerization of $(\text{EMM}-)_{2}\text{Cr}(\text{OH})$ -vinyl monomers: (O) $(\text{EMM}-)_{2}\text{Cr}(\text{OH})$ 5 wt-%, MMA-HEMA (10/1) 95 wt-%; (●) $(\text{EMM}-)_{2}\text{Cr}(\text{OH})$ 15.4 wt-%, MMA-HEMA (10/1) 84.6 wt-%; (□) $(\text{EMM}-)_{2}\text{Cr}(\text{OH})$ 5 wt-%, St-HEMA (10/1) 95 wt-%; (■) $(\text{EMM}-)_{2}\text{Cr}(\text{OH})$ 15.4 wt-%, St-HEMA (10/1) 84.6 wt-%.

this constant ratio was dissolved $(\text{EMM}-)_{2}\text{Cr}(\text{OH})$ in various quantities and the compositions were copolymerized.

Figure 1 shows the time-conversion curves for the copolymerization of $(\text{EMM}-)_{2}\text{Cr}(\text{OH})$ -MMA-HEMA and $(\text{EMM}-)_{2}\text{Cr}(\text{OH})$ -St-HEMA. The first-step polymerizations were carried out at 55°C for 10 hr. In all systems, the rates of copolymerization increased markedly as the concentration of $(\text{EMM}-)_{2}\text{Cr}(\text{OH})$ increased. This tendency is considered to be due to the "gel effect." Besides, the rates of polymerization of the $(\text{EMM}-)_{2}\text{Cr}(\text{OH})$ -MMA-HEMA system are much higher than those of the $(\text{EMM}-)_{2}\text{Cr}(\text{OH})$ -St-HEMA system, and at 55°C conversion reached nearly the maximum conversion attainable after about 5-7 hr. Such a tendency was observed also in the previous studies.^{1,5} In the $(\text{EMM}-)_{2}\text{Cr}(\text{OH})$ -St-HEMA system, conversion did not reach the maximum conversion attainable even after 10 hr. Successively, the second-step polymerizations were carried out at 100°C, and, as a result, it was found that the conversion at high concentration of $(\text{EMM}-)_{2}\text{Cr}(\text{OH})$ reached the maximum conversion attainable within 1 hr, whereas when the concentration of $(\text{EMM}-)_{2}\text{Cr}(\text{OH})$ was low, conversion did not reach the maximum conversion attainable even after 5 hr.

In all systems, the observed gelation of the polymerization systems occurred at 5-10% conversion. Moreover, at the beginning of 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 25% conversion. The copolymers obtained were deep blue, hard materials.

According to the results of the copolymerization mentioned above, the polymerization condition for obtaining samples for determining physical properties was set up as follows: For the $(\text{EMM}-)_{2}\text{Cr}(\text{OH})$ -MMA-HEMA system, 55°C for 10 hr, 100°C for 5 hr, 110°C for 2 hr. For the

(EMM—)₂Cr(OH)—St-HEMA system, 55°C for 15 hr, 80°C for 4 hr, 100°C for 5 hr, 110°C for 2 hr.

Physical Properties of Copolymers

The compositions of the copolymers used for determining physical properties were as follows: The concentration of (EMM—)₂Cr(OH) was below 15.4 wt-% in the copolymers of (EMM—)₂Cr(OH)—MMA-HEMA, and below 10 wt-% in the copolymers of (EMM—)₂Cr(OH)—St-HEMA. The weight ratio of MMA or St and HEMA was 10:1.

HDT. As shown in Figure 2, in the copolymers of (EMM—)₂Cr(OH)—MMA-HEMA, HDT has a minimum value at 5% (EMM—)₂Cr(OH). Such a tendency was not observed in the copolymers of the Cr salt of EMP-MMA in the previous study.² On the other hand, in the copolymers of (EMM—)₂Cr(OH)—St-HEMA, HDT increases gradually with increase in (EMM—)₂Cr(OH); for instance, a 4°C increase is observed at 10% (EMM—)₂Cr(OH).

Tensile Strength. As is clear from Figure 2, in all copolymers tensile strength has a peak at 5% (EMM—)₂Cr(OH). For instance, in the copolymers of (EMM—)₂Cr(OH)—MMA-HEMA, a high value of 870 kg/cm² (an approximate 100 kg/cm² increase) was observed.

Rockwell Hardness. As shown in Figure 3, in all copolymers Rockwell hardness increases with increase in (EMM—)₂Cr(OH), particularly the rate of increase in the copolymers of (EMM—)₂Cr(OH)—St-HEMA is high. Thus, the effect of introducing (EMM—)₂Cr(OH) appears in the Rockwell hardness.

Flexural Strength. As is clear from Figure 3, in the copolymers of (EMM—)₂Cr(OH)—MMA-HEMA, flexural strength reaches a minimum value of about 700 kg/cm² at 10% (EMM—)₂Cr(OH). However, it is

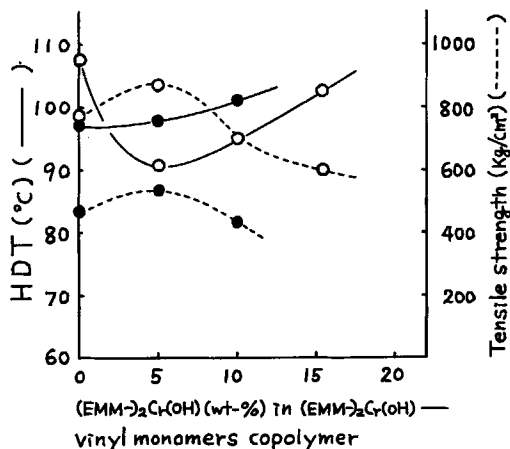


Fig. 2. Effect of (EMM—)₂Cr(OH) on HDT and tensile strength of (EMM—)₂Cr(OH)—vinyl monomers copolymer: (○) (EMM—)₂Cr(OH)—MMA-HEMA; (●) (EMM—)₂Cr(OH)—St-HEMA. Weight ratio of MMA or St/HEMA = 10/1.

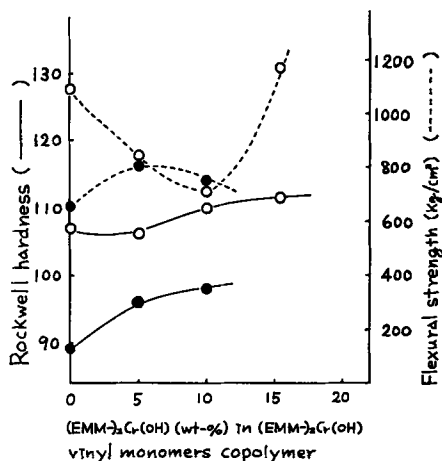


Fig. 3. Effect of $(\text{EMM}-)_2\text{Cr}(\text{OH})$ on Rockwell hardness and flexural strength of $(\text{EMM}-)_2\text{Cr}(\text{OH})$ -vinyl monomers copolymer: (O) $(\text{EMM}-)_2\text{Cr}(\text{OH})$ -MMA-HEMA; (●) $(\text{EMM}-)_2\text{Cr}(\text{OH})$ -St-HEMA. Weight ratio of MMA or St/HEMA = 10/1.

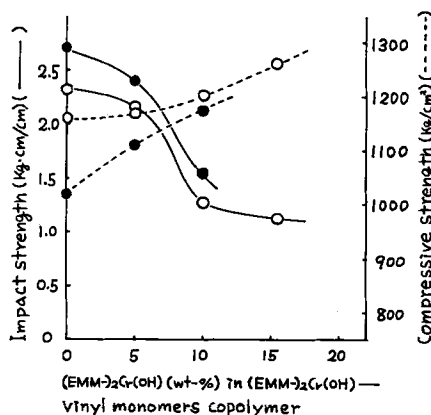


Fig. 4. Effect of $(\text{EMM}-)_2\text{Cr}(\text{OH})$ on impact strength and compressive strength of $(\text{EMM}-)_2\text{Cr}(\text{OH})$ -vinyl monomers copolymer: (O) $(\text{EMM}-)_2\text{Cr}(\text{OH})$ -MMA-HEMA; (●) $(\text{EMM}-)_2\text{Cr}(\text{OH})$ -St-HEMA. Weight ratio of MMA or St/HEMA = 10/1.

noteworthy that flexural strength reaches a high value of about 1170 kg/cm² at 15.4% $(\text{EMM}-)_2\text{Cr}(\text{OH})$. On the other hand, in the copolymers of $(\text{EMM}-)_2\text{Cr}(\text{OH})$ -St-HEMA, flexural strength reaches a peak at 5% $(\text{EMM}-)_2\text{Cr}(\text{OH})$, at which an about 140 kg/cm² increase is observed, and in this case the effect of introducing $(\text{EMM}-)_2\text{Cr}(\text{OH})$ appears.

Impact Strength. As is clear from Figure 4, in all copolymers impact strength decreases markedly with increase in $(\text{EMM}-)_2\text{Cr}(\text{OH})$. On the other hand, in the copolymers of the Cr salt of EMP-St, impact strength has a peak of 2.96 kg-cm/cm at 5% Cr salt.² However, such a tendency was not observed in the present study.

Compressive Strength. As shown in Figure 4, in all copolymers compressive strength increases with increase in $(\text{EMM})_2\text{Cr}(\text{OH})$, particularly the rate of increase in the copolymers of $(\text{EMM})_2\text{Cr}(\text{OH})$ -St-HEMA is high. In the copolymers of $(\text{EMM})_2\text{Cr}(\text{OH})$ -MMA-HEMA, compressive strength reaches a high value of about 1270 kg/cm^2 at 15.4% $(\text{EMM})_2\text{Cr}(\text{OH})$. Thus, in compressive strength, too, the effect of introducing $(\text{EMM})_2\text{Cr}(\text{OH})$ appears clearly.

In summary of the results described above, the following may be concluded. Generally, Rockwell hardness and compressive strength can be improved by introducing $(\text{EMM})_2\text{Cr}(\text{OH})$ into the polymers, and HDT, tensile, and flexural strengths can also be improved by selecting the most suitable concentration of $(\text{EMM})_2\text{Cr}(\text{OH})$ according to the species of vinyl monomers. On the other hand, impact strength has a tendency to decrease when $(\text{EMM})_2\text{Cr}(\text{OH})$ is introduced.

TGA

Figure 5 shows the TGA curves for the representative copolymers. The decomposition temperature was defined, in the same way as in the previous report,⁵ 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 $(\text{EMM})_2\text{Cr}(\text{OH})$ -MMA-HEMA and blank polymer (MMA-HEMA) showed decomposition temperatures of 244°C and 245°C , respectively, and temperatures at 50% loss of 307°C and 302°C , respectively. The thermal stability of this copolymer is not influenced by $(\text{EMM})_2\text{Cr}(\text{OH})$. In the previous study,¹ it was observed that introducing the Mg or Ca salt of EMM into the MMA-HEMA copolymer increased the thermal stability. On the other hand, the copolymer of $(\text{EMM})_2\text{Cr}(\text{OH})$ -St-HEMA and blank polymer (St-HEMA) showed decomposition temperatures of 266°C and 290°C , respectively, and temperatures at 50% loss of 327°C and 345°C , respectively. From this it is

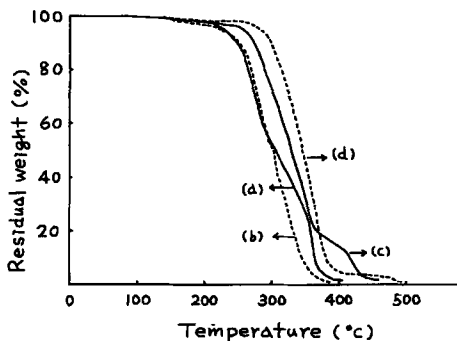


Fig. 5. TGA curves of copolymers obtained: (a) $(\text{EMM})_2\text{Cr}(\text{OH})$ (15.4 wt-%)-MMA-HEMA; (b) blank polymer (MMA-HEMA); (c) $(\text{EMM})_2\text{Cr}(\text{OH})$ (10 wt-%)-St-HEMA; (d) blank polymer (St-HEMA).

apparent that the introduction of $(\text{EMM—})_2\text{Cr}(\text{OH})$ into the St-HEMA copolymer decreases the thermal stability a little. A similar tendency was observed in the copolymer of the Cr salt of EMP-St in the previous study.²

Boiling Water Resistance

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

In the copolymers containing $(\text{EMM—})_2\text{Cr}(\text{OH})$, the surfaces of the samples showed no change. Similarly, the blank polymer (MMA-HEMA) showed no change. However, in the blank polymer (St-HEMA), the surface became white.

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

Generally, the boiling water resistance of the copolymers in the present study is higher than that of the copolymers containing the Mg or Ca salt of EMM in the previous study.¹ This may be attributed to the degree of ionic character. That is, the copolymers containing $(\text{EMM—})_2\text{Cr}(\text{OH})$ are considered to have a lower ionic character than those containing the Mg or Ca salt of EMM.

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