

Studies of Reactions with Polymers. III. Syntheses and Properties of Poly(vinyl Alcohol) Graft Terpolymers

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Synopsis

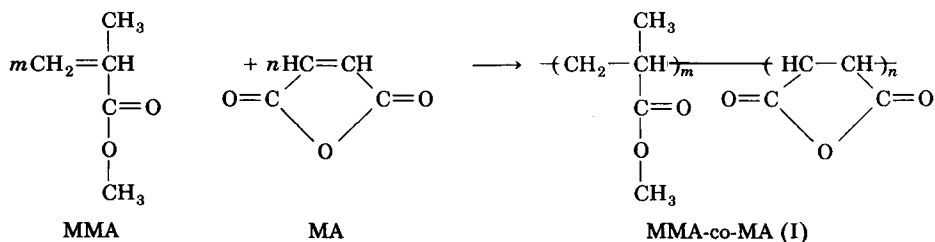
A condensation-coupling reaction through esterification is performed between the hydroxy groups of poly(vinyl alcohol) (PVA) and the anhydride groups of methyl methacrylate (MMA)-co-maleic anhydride (MA) copolymer to produce the PVA-*g*-MMA/MA graft terpolymer. The MMA-co-MA copolymer was obtained by copolymerization of MA and MMA in dimethyl sulfoxide by using azobisisobutyronitrile as initiator. The structure of reaction products was confirmed by infrared analysis, and the dependence of composition, viscosity, and yield of the graft terpolymer on the MA content in MMA-co-MA as well as the concentration of the reactants fed were investigated. Mechanical properties, water content, and gel content of the membranes of terpolymers were measured over a wide range of compositions. PVA-*g*-MMA/*N*-ethylol maleimide was also synthesized by reacting the residual anhydride groups on PVA-*g*-MMA/MA with ethanol amine, this reaction proceeds through the PVA-*g*-MMA/*N*-ethylol maleamic acid intermediate.

INTRODUCTION

In previous papers,^{1,2} we reported the synthesis of PVA graft copolymers to improve the water resistance of PVA by grafting maleic anhydride (MA) and acrylonitrile (AN) using potassium persulfate (KPS) as an initiator. It was found that the MA in the side chain would rearrange to form a keto-olefinic structure.

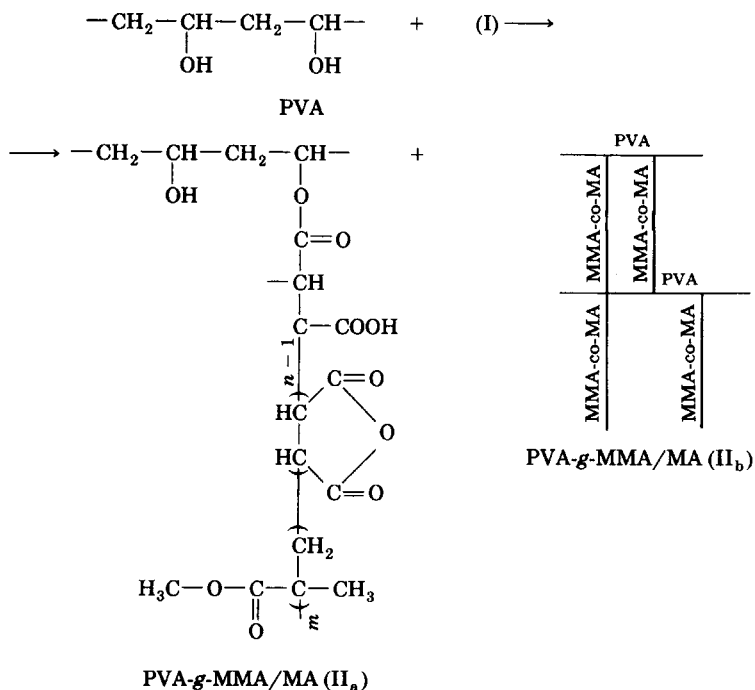
Graft copolymers have been generally synthesized either by polymerization a monomer from an initiating site on a backbone or by linking two different polymers through a polymer reaction.³⁻⁶ Since it is impossible to synthesize the grafted side chains with an anhydride structure by grafting MA onto PVA by using former grafting method, this paper presents the synthesis and properties of PVA graft copolymers containing anhydride side chains.

A copolymer of MMA and MA was prepared in the first stage as follows:



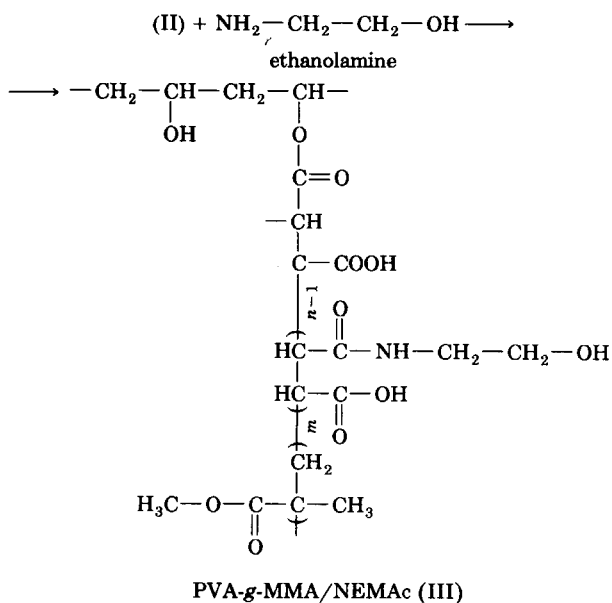
Reaction 1.

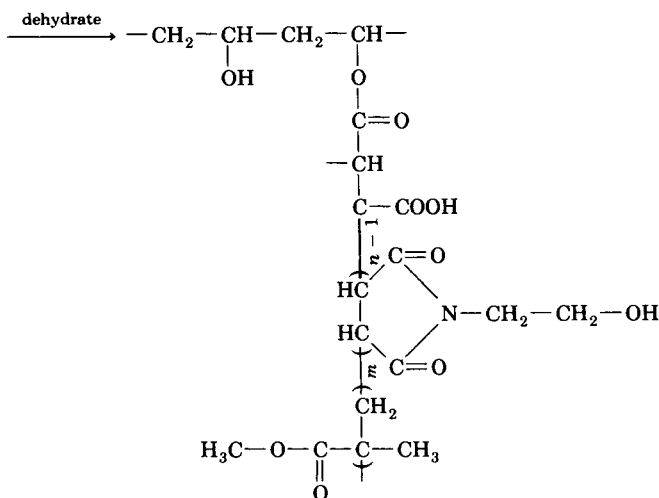
The coupling reaction between the backbone hydroxy groups and the MMA-co-MA anhydride groups was carried out in the second stage:



Reaction 2.

PVA-g-MMA/*N*-ethylol maleimide (NEMI) was prepared in a third step by reacting the residual anhydride groups in the side chain of PVA-g-MMA/MA with ethanolamine, dehydrating the resulting PVA-g-MMA/*N*-ethylol maleamic acid (NEMAc), and converting to the obtained PVA-g-MMA/NEMI:



PVA-*g*-MMA/NEMI (IV)

Reaction 3.

EXPERIMENTAL

Material

PVA BF-17, a product of Chang Chun Petrochemical Co., Taiwan, DP = 1700, degree of saponification of 98.5–99.2 mol % and viscosity of 25–30 cp was used. MA, MMA, and DMSO of reagent grades were purchased from Wako Pure Chemical Industries. MMA was washed with aqueous sodium hydroxide and distilled water, neutralized with hydrochloric acid. It was then refluxed and distilled over calcium hydride and hydroquinone. Azobisisobutyronitrile (AIBN) of a reagent grade used as the initiator was purchased from Nakarai Chemical Co., Japan. Solvents such as toluene, methanol, and acetone were used without further purification.

Copolymerization of MMA and MA (Reaction 1)

The copolymerization reaction was carried out in a four-necked flask equipped with a stirrer, thermometer, condenser, and nitrogen inlet. The general experimental procedure and an example were as follows: MMA 50 g and MA 48 g were dissolved in 20 mL DMSO after being stirred in an atmosphere of nitrogen. The reaction temperature was adjusted at 70°C, and 1 g AIBN was added as an initiator. The reaction was allowed to proceed for 5 h. The products were precipitated in a large methanol excess and dried in a vacuum oven below 30°C.

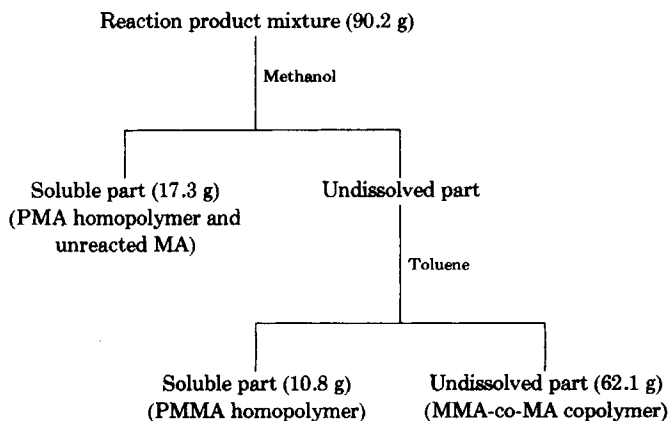
Coupling Reaction between MMA-co-MA and PVA (Reaction 2)

MMA-co-MA (10 g) prepared as described above was dissolved in DMSO (120 mL), and, after complete dissolution, PVA was added. The reaction was

allowed to react at 100°C for 24 h, with mechanical stirring under nitrogen. The products were precipitated in water.

Purification of Copolymer

The products precipitated from methanol in Reaction 1 were a mixture of MMA-co-MA copolymer and unreacted MA, as well as homopolymer of MMA and MA. They were separated and purified as introduced:



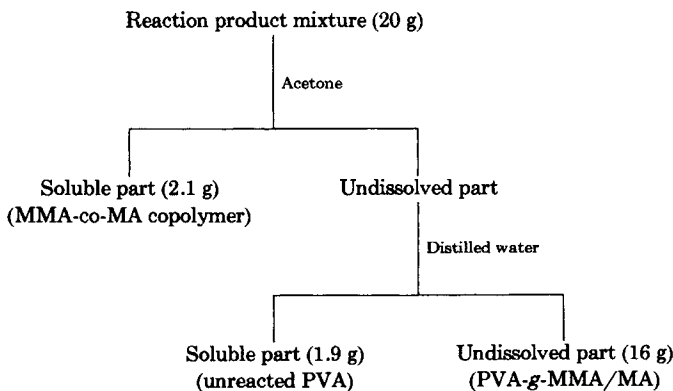
After the separation, all materials must be dried in a vacuum below 30°C. The composition of MMA-co-MA was calculated as follows:

$$\text{wt \% of MA in copolymer} = \frac{(A)}{\text{wt of MA feed}} \times 100\%$$

$$(A) = \text{wt of MA feed} - (\text{wt of MA homopolymer} + \text{wt of unreacted MA})$$

$$\text{wt \% of MMA in copolymer} = 100\% - \text{wt \% of MA in copolymer}$$

The products precipitated from water in Reaction 2 were a mixture of grafted terpolymer PVA-*g*-MMA/MA, unreacted PVA, and unreacted MMA-co-MA. They were separated and purified as shown:



After the separation, all materials must be dried in a vacuum below 30°C. Data of grafting terpolymerization were calculated as follows:

wt % of MA in graft terpolymer

$$= \frac{(B) \times (\text{wt \% of MA in MMA-co-MA})}{\text{wt of PVA-g-MMA/MA}} \times 100\%$$

$$(B) = \text{wt of MMA-co-MA feed} - \text{wt of unreacted MMA-co-MA}$$

wt % of MMA in graft terpolymer

$$= \frac{(B) \times (\text{wt \% of MMA in MMA-co-MA})}{\text{wt of PVA-g-MMA/MA}} \times 100\%$$

wt % of PVA in graft terpolymer

$$= \frac{\text{wt of PVA feed} - \text{wt of unreacted PVA}}{\text{wt of PVA-g-MMA/MA}} \times 100\%$$

$$= 100\% - (\text{wt \% of MA in PVA-g-MMA/MA} + \text{wt \% of MMA in PVA-g-MMA/MA})$$

The Synthesis of PVA-g-MMA / NEMI (Reaction 3)

PVA-g-MMA/MA was dissolved in DMSO, and excess ethanolamine was added. The reaction proceeds at a temperature of 60°C. After reaction, the solution was cast into PVA-g-MMA/NEMAc membrane at 30°C in vacuum and further converted to PVA-g-MMA/NEMI membrane by gradually heating to 150°C in vacuum.

Preparation of Membrane of Graft Copolymer

Membranes were prepared from about 30% solution of the graft terpolymer in DMSO. The solution was cast over a clean glass plate which was allowed to dry at 30–40°C in a vacuum to constant weight before the membrane was removed from the plate.

Measurement of Various Properties

Viscosity

The intrinsic viscosities of PVA, MMA-co-MA, and PVA-g-MMA/MA were determined in DMSO in an Ubbelohde viscometer at 30°C, by extrapolating of η_{sp}/c to $c = 0$.

Infrared Spectra

IR spectra were obtained from films or in mixtures with KBr on a JASCO Model A-202 spectrophotometer.

Gel Content

After heat treatment the membranes of graft terpolymers were extracted with DMSO at boiling temperature for 24 h, and residual terpolymers were dried and weighted. Gel content was calculated using

$$\text{gel content (\%)} = \frac{\text{wt of membrane after extraction}}{\text{wt of original membrane}} \times 100\%$$

Water Content

Membranes were first immersed in boiling water for 6 h and then removed. The membranes were superficially dried with filter paper and weighted. Water content was calculated using

$$\text{water content (\%)} = \frac{\text{wt of membrane after absorption water}}{\text{wt of original membrane}} \times 100\%$$

Mechanical Properties

The tensile strength and elongation at break of membranes were determined by the ASTM D-638 test method by Instron Model 1130.

Thermal Analysis

TGA and DSC measurement were performed on a DuPont Instruments 1090B analyzer. TGA was measured on 951 thermogravimetric analyzer at a heating rate of 20°C/min in a nitrogen atmosphere at a flow rate of 100 mL/min. DSC was measured on a 910 differential scanning calorimeter at a heating rate of 10°C/min in a nitrogen atmosphere at a flow rate of 30 mL/min.

RESULTS AND DISCUSSION

MMA-co-MA

Table I shows that the intrinsic viscosity and the yield of MMA-co-MA decrease when concentration of MA in feed increases. This monomer has a strong tendency to chain transfer,^{7,8} and the decrease of viscosity can be attributed to the transfer reactions during copolymerization. For the same reason, the introduction of a smaller amount of MA into the monomer feed produces a copolymer relatively rich in MA. It shows some tendency for the predominance of MA units in the copolymer, and the copolymer does not attain a fully alternating structure.

PVA-g-MMA / MA

The major difficulty encountered in the synthesis of this graft terpolymer was gel formation, due to the presence of many anhydride groups in the

TABLE I
Effect of Monomer Feed on Composition, Yield, and Intrinsic Viscosity of Copolymer

Monomer feed ^a (mole fraction)		Copolymer composition (mole fraction)		Yield (%)	Intrinsic ^b viscosity (dL/g)
MMA	MA	MMA	MA		
0.50	0.50	0.47	0.53	63.4	0.073
0.60	0.40	0.54	0.46	67.2	0.080
0.75	0.25	0.65	0.35	68.3	0.103
0.85	0.15	0.74	0.26	72.6	0.122
1.00	0.00	1.00	0.00	92.6	0.164

^aAIBN (g) = (MMA + MA) (g) × 0.01; DMSO (g) = (MMA + MA) (g) × 0.2.

^bT = 30°C; solvent DMSO.

MMA-co-MA copolymer and many hydroxy groups in PVA backbone. It was found that gelation would occur when PVA/MMA-co-MA (wt ratio) > 2. Attempts were made to minimize the problem by properly adjusting the total initial concentration of reactants.

The effect of the wt % of PVA in feed on the composition of PVA-g-MMA/MA is shown in Figure 1. Increasing the PVA feed (wt %) results in an

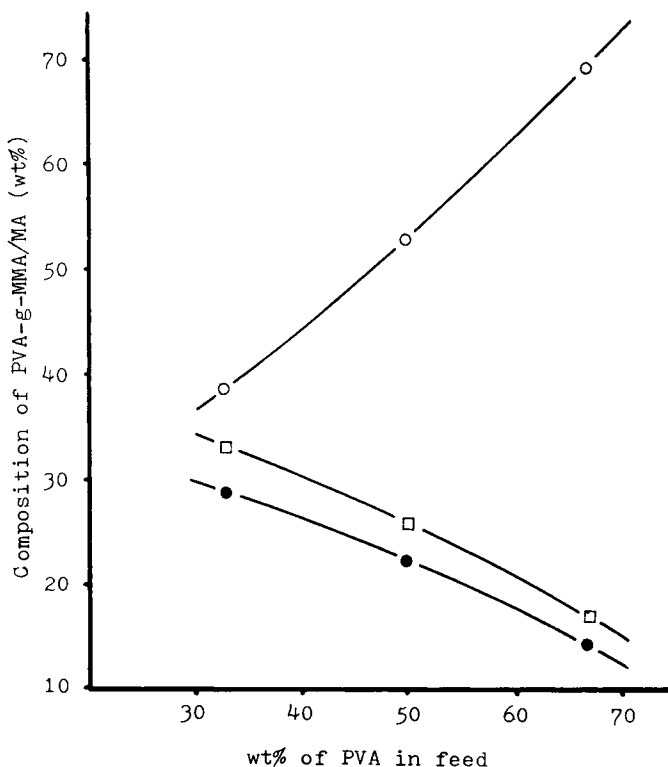


Fig. 1. Effect of the wt % of PVA in feed on the composition of PVA-g-MMA/MA (MMA-co-MA; mole fraction 0.47 : 0.53): (○) wt % of PVA in terpolymer; (□) wt % of MA in terpolymer; (●) wt % of MMA in terpolymer.

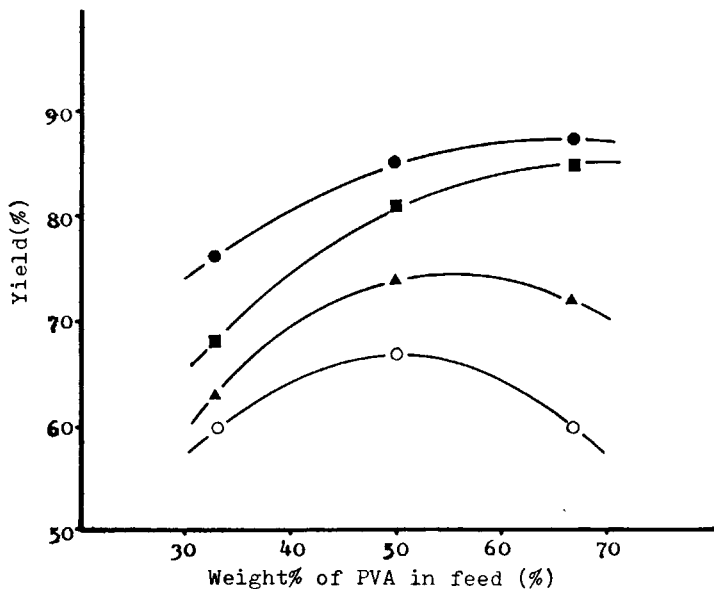


Fig. 2. Effect of the wt % of PVA in feed on the yield of product. Mole fraction of MMA-co-MA: (●) 0.47:0.53; (■) 0.54:0.46; (▲) 0.65:0.35; (○) 0.74:0.26.

increase of PVA content, but a decrease of MA and MMA content in PVA-*g*-MMA/MA.

The yield of PVA-*g*-MMA/MA increases to a maximum, and then decreases with increasing PVA feed wt % by using the MMA-co-MA with lower MA content (Fig. 2). This is due to the lower MA content in MMA-co-MA, which should have lower reactivity with PVA since it contains less anhydride groups, resulting in a sharp increase of unreacted PVA at higher PVA feed wt %.

It should point out that the MA content in PVA-*g*-MMA/MA (Fig. 1) is not all present as anhydride; some anhydride groups are converted into ester groups by esterification with PVA. The mole ratio (M) of the residual

TABLE II
The Value of M after the Coupling Reaction of PVA with MMA-co-MA

Copolymer composition (mole fraction)		PVA feed (wt %)	$x_1/(x_1 + x_2)/(M)$
MMA	MA		
0.47	0.53	33.3	0.58
		50.0	0.44
		66.7	0.35
0.54	0.46	33.3	0.54
		50.0	0.42
		66.7	0.31
0.65	0.35	33.3	0.57
		50.0	0.45
		66.7	0.30

anhydride units in PVA side chain to the original anhydride units in MMA-co-MA is measured by infrared spectroscopy.⁹

For PVA-*g*-MMA/MA graft terpolymer:

$$A_1 = a_{11}x_1 + a_{12}x_2 + a_{13}x_3 + a_{14}x_4 \quad (1)$$

$$A_2 = a_{21}x_1 + a_{22}x_2 + a_{23}x_3 + a_{24}x_4 \quad (2)$$

where A_1 = the integral absorbance of the anhydride carbonyl extended from 1923 to 1770 cm^{-1} , A_2 = the integral absorbance of the ester and/or acid carbonyl extended from 1770 to 1667 cm^{-1} , x_1 , x_2 , x_3 , and x_4 = mol/L of succinic anhydride, succinate, methyl methacrylate, and vinyl acetate groups, respectively, and a_{ij} = the absorptivity of group type j at band i .

The absorbance of PVA in this region could be ignored because the almost hydrolyzed PVA shows about no carbonyl absorption; thus

$$a_{14} = a_{24} = 0 \quad (3)$$

The integral absorbance of MMA in region A_1 is equal to zero:

$$a_{13} = 0 \quad (4)$$

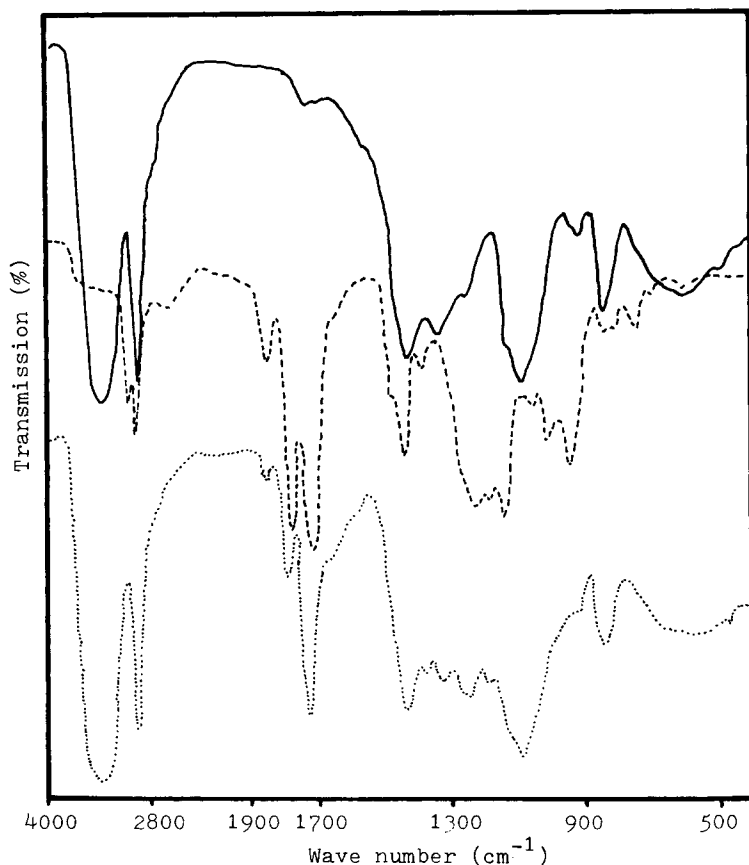


Fig. 3. IR spectra of: (---) MMA-co-MA; (—) PVA; (···) PVA-*g*-MMA/MA.

The mole ratio (F) of MA to MMA in MM-co-MA copolymer could be obtained from Table I:

$$(x_1 + x_2)/x_3 = F \quad (5)$$

The value of M could be solved by combining eqs. (1)–(5).

$$M = x_1/(x_1 + x_2) = (C)/(C) + (D)$$

$$(C) = a_{23}A_1 + a_{22}A_1F - a_{12}A_2F$$

$$(D) = a_{11}A_2F - a_{21}A_1F$$

The results are shown in Table II. The value of M decreases with increasing PVA feed wt %.

Figure 3 shows the IR spectra of MMA-co-MA, PVA, and PVA-*g*-MMA/MA. The IR spectrum of PVA-*g*-MMA/MA contains the characteristic band of anhydride groups (1860 and 1780 cm^{-1}) and carbonyl groups (1735 cm^{-1}) from the grafted MMA-co-MA side chain.

Properties of Graft Terpolymer

A plot of intrinsic viscosity $[\eta]$ of PVA-*g*-MMA/MA against the PVA feed wt % and MA content in MMA-co-MA is shown in Figure 4. With increasing the MA content in MMA-co-MA, there is a marked increase in $[\eta]$. As

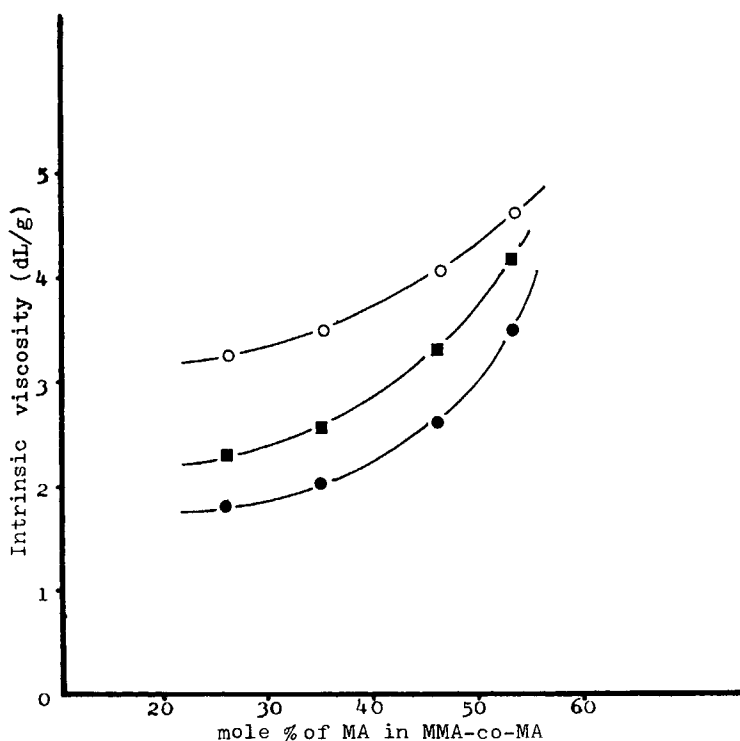


Fig. 4. Effect of the mol % of MA in MMA-co-MA on the intrinsic viscosity of PVA-*g*-MMA/MA. Wt % of PVA in feed: (○) 66.7; (■) 50.0; (●) 33.3.

mentioned above, MMA-co-MA with higher MA content should have higher reactivity with PVA, so that this increase of $[\eta]$ could be explained by an increase of the number of grafted side chain. It should be noted that the $[\eta]$ of PVA-g-MMA/MA is more than twice the $[\eta]$ of original PVA (1.5 dL/g) when the higher MA content copolymer was used, and this result reflects that one graft terpolymer molecular could contain more than one PVA backbone as proposed structure (II_b).

PVA-g-MMA/MA formed a crosslinking network as a result of the inter-chain ester linkage during the heat treatment, as proposed below:

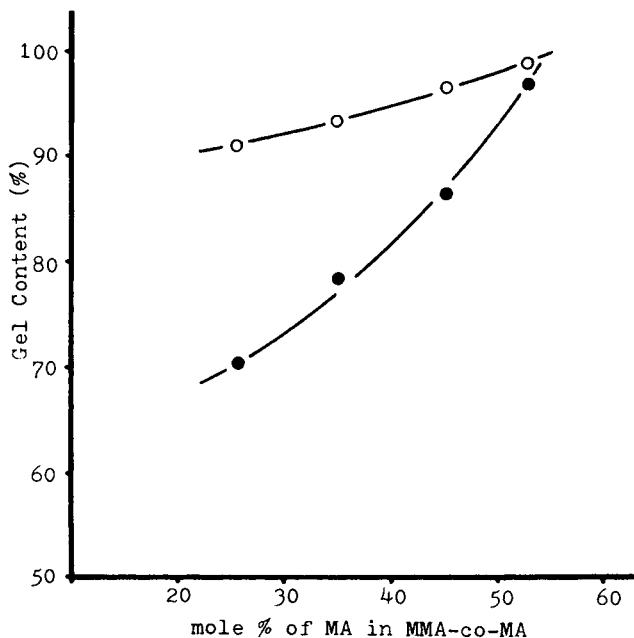
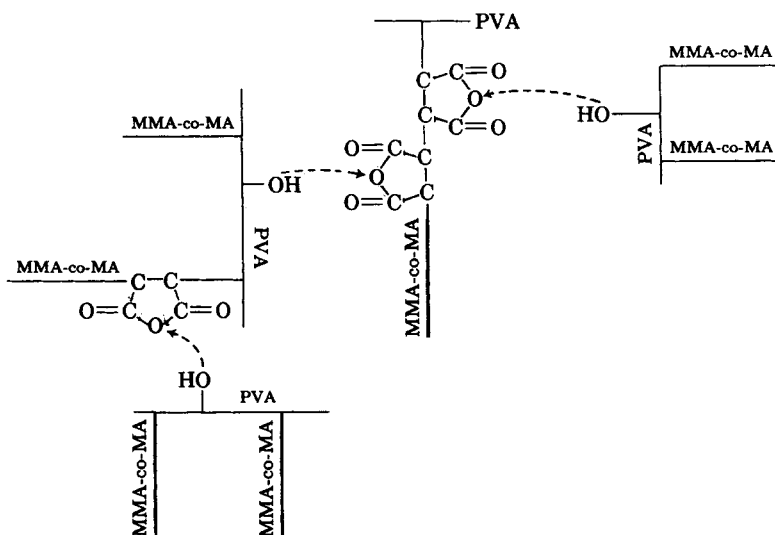


Fig. 5. Effect of the mol % of MA in MMA-co-MA on the gel content of PVA-g-MMA/MA after heat treatment (carried out at 100°C for 3 h). Wt % of PVA in feed: (○) 50.0; (●) 33.3.

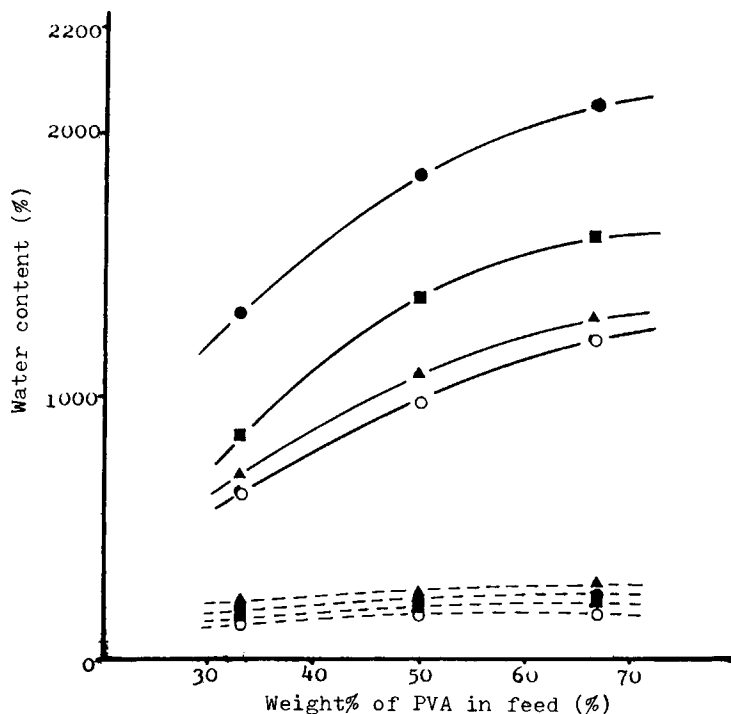


Fig. 6. Effect of the wt % of PVA in feed on water content of PVA-g-MMA/MA [(—) before heat treatment; (---) after heat treatment]. Heat treatment was carried out at 100°C for 3 h. Mole fraction of MMA-co-MA: (●) 0.47 : 0.53; (■) 0.54 : 0.46; (▲) 0.65 : 0.35; (○) 0.74 : 0.26.

Similar ester linkage involving polyacid and PVA has been reported in the literature.^{10,11} It was concluded that 3 h at 100°C was sufficient to develop fully the ester linkage. Figure 5 shows that the gel content of PVA-g-MMA/MA depends directly on the amount of anhydride groups within it.

That PVA-g-MMA/MA has a higher water content (above 1000%) results from the much more hydrophilic groups (hydroxy, acid, and anhydride groups) within it. The water content decreases to about 200% after heat treatment because of the intermolecular crosslinking and the decrease in hydrophilic groups (Fig. 6).

The effect of PVA feed wt % on mechanical properties of the PVA-g-MMA/MA membranes are shown in Figures 7 and 8. PVA is a crystalline polymer with high tensile strength, but MMA-co-MA is an amorphous copolymer. Therefore, the tensile strength increases whereas the elongation at break decreases before heat treatment in dry state with increasing the PVA feed wt %. The high water content of PVA-g-MMA/MA results in poor mechanical properties before heat treatment in the wet state. After heat treatment, it shows a higher tensile strength in dry and wet states for the intermolecular crosslinking.

Thermograms from TGA are shown in Figure 9. They show that the graft terpolymer has better thermal resistance and higher residual weights than PVA and MMA-co-MA, and this could be due to the higher molecular weight of PVA-g-MMA/MA and the occurrence of interchain ester linkage during

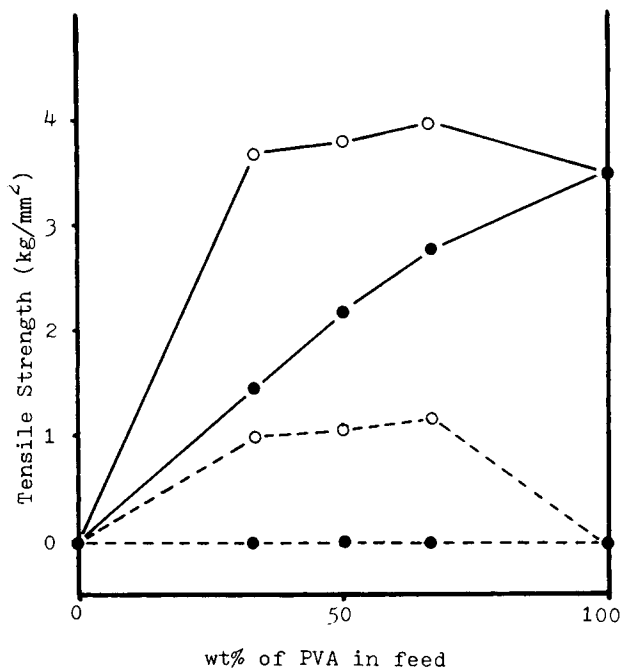


Fig. 7. Effect of the wt % of PVA in feed on tensile strength of PVA-g-MMA/MA(MMA-co-MA; mole fraction 0.47:0.53). Membrane in dry state: (—●—) before heat treatment; (—○—) after heat treatment. Membrane in wet state: (—●—) before heat treatment; (—○—) after heat treatment. Heating temperature-100°C; heating time = 3 h.

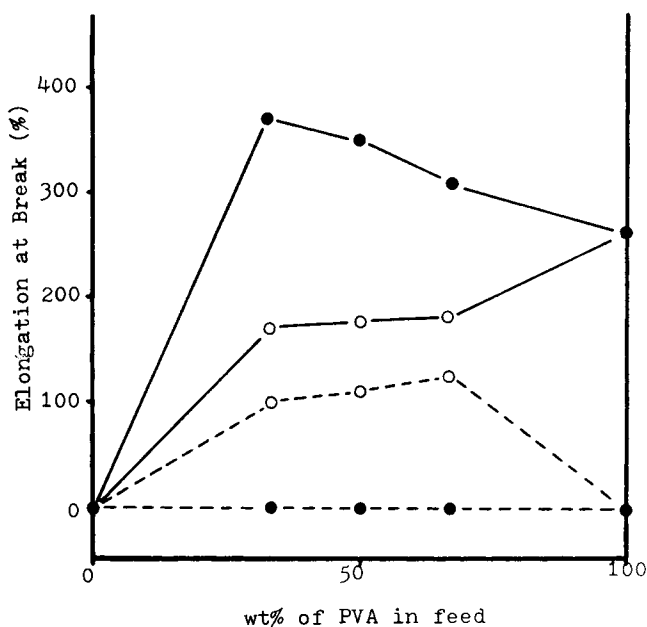


Fig. 8. Effect of the wt % of PVA in feed on elongation at break of PVA-g-MMA/MA(MMA-co-MA; mole fraction 0.47:0.53). Membrane in dry state: (—●—) before heat treatment; (—○—) after heat treatment. Membrane in wet state: (—●—) before heat treatment; (—○—) after heat treatment. Heating temperature = 100°C; heating time = 3 h.

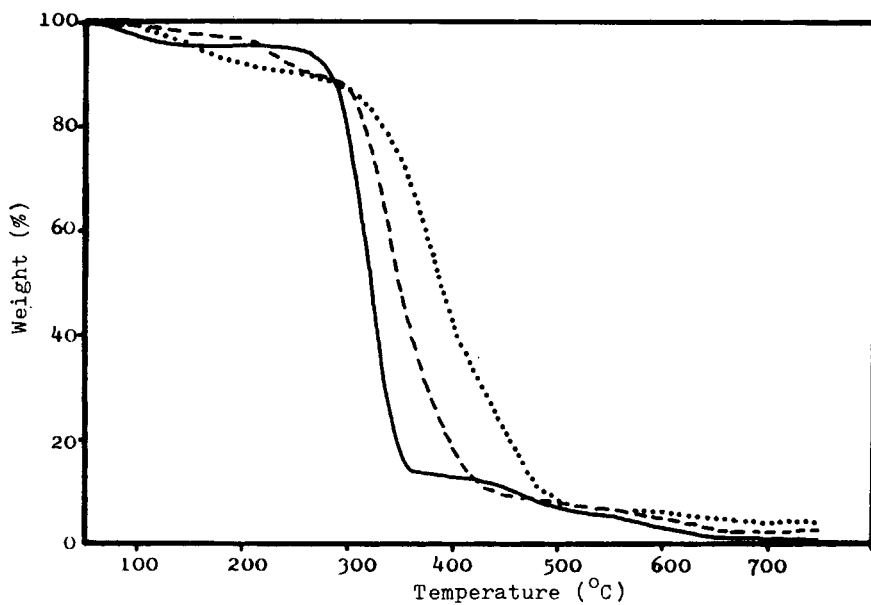


Fig. 9. TGA thermogram of (—) PVA; (---) MMA-co-MA; (···) PVA-g-MMA/MA. MMA-co-MA, mole fraction 0.47:0.53; PVA feed wt% = 50%.

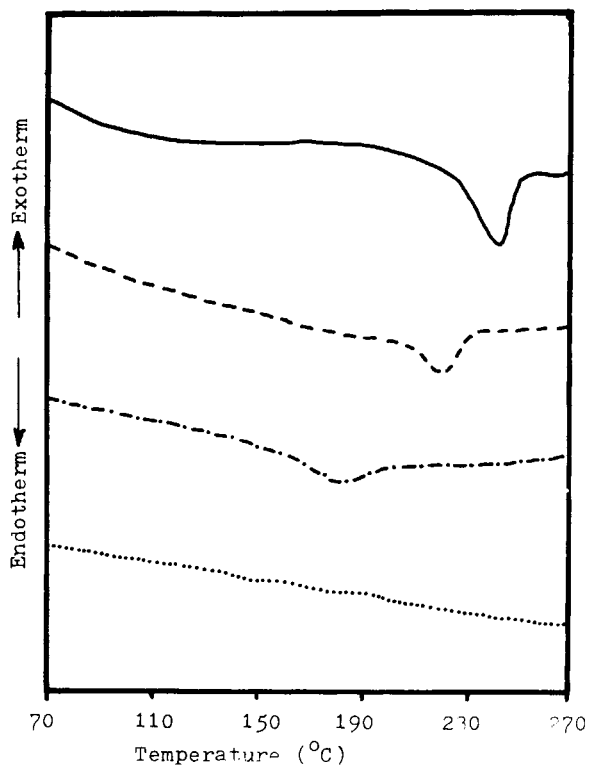


Fig. 10. DSC thermogram of (—) PVA; (···) MMA-co-MA; PVA-g-MMA/MA: (---) PVA feed wt % = 50; (-·-·) PVA feed wt % = 33.3. MMA-co-MA, mole fraction 0.47:0.53.

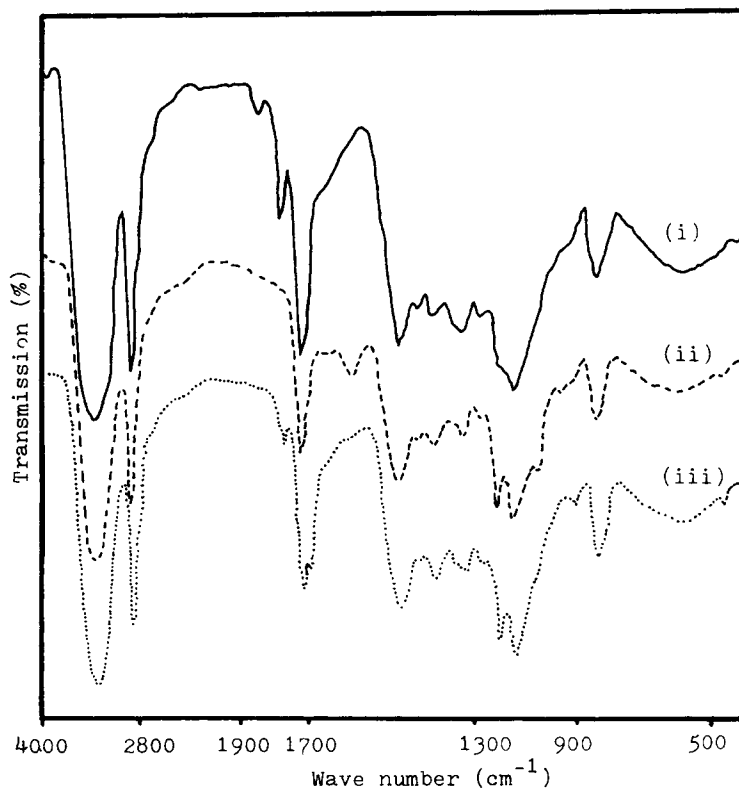


Fig. 11. IR spectra of (—) PVA-*g*-MMA/MA; (---) PVA-*g*-MMA/NEMAc; (···) PVA-*g*-MMA/NEMI.

the heating treatment. DSC curves of MMA-co-MA, ungrafted and grafted PVA samples (Fig. 10) indicate that the MMA-co-MA is an amorphous polymer, and PVA is a crystalline polymer. From the curves it is obvious that the melting point endotherm of PVA-*g*-MMA/MA decreases with increasing the PVA feed wt %.

PVA-*g*-MMA/NEMI

The IR spectra of PVA-*g*-MMA/MA, PVA-*g*-MMA/NEMAc, and PVA-*g*-MMA/NEMI are shown in Figure 11. The major differences between (i) and (iii) in Figure 11 found in the carbonyl stretching region: The anhydride absorption 1860 and 1780 cm^{-1} disappears, and a new absorption peak of the imide (1770 and 1705 cm^{-1}) occurs.

CONCLUSIONS

In the condensation-coupling through esterification of PVA and MMA-co-MA, it was found that the MMA-co-MA with higher MA content had a higher reactivity with PVA. The grafted terpolymers showed a higher water resistance and better mechanical properties than the PVA after heat treatment, due to the occurrence of interchain ester linkages.

The residual anhydride groups on the side chain of PVA-*g*-MMA/MA could be reacted further with other monomers (ethanolamine, *N*-alkyl amine) to produce new PVA graft copolymers. This will be reported in our next paper.

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References

1. W. Y. Chiang and C. M. Hu, *J. Appl. Polym. Sci.*, **30**, 3895 (1985).
2. W. Y. Chiang and C. M. Hu, *J. Appl. Polym. Sci.*, **30**, 4045 (1985).
3. L. Akcelrud and A. S. Gomes, *J. Polym. Sci., Polym. Chem. Ed.*, **24**, 2831 (1986).
4. Y. Ikada, H. Iwata, and T. Mita, *Macromolecules*, **12**, 808 (1979).
5. A. G. Deboos and G. Allen, *Polymer*, **16**, 38 (1975).
6. Y. Ikada, K. Maejima, and H. Iwata, *Makromol. Chem.*, **179**, 865 (1978).
7. R. M. Joshi, *Makromol. Chem.*, **53**, 33 (1962).
8. R. M. Joshi, *Makromol. Chem.*, **55**, 35 (1962).
9. E. L. Saier, L. Petrakis, and L. R. Cousins, *J. Appl. Polym. Sci.*, **12**, 2191 (1968).
10. C. E. Reid and H. G. Spencer, *J. Appl. Polym. Sci.*, **4**, 354 (1960).
11. C. C. Gryte, J. Chen, V. Kevorkian and H. P. Gregor, *J. Appl. Polym. Sci.*, **23**, 2611 (1979).

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