Studies of Reactions with Polymers. I. The Reaction of Maleic Anhydride with PVA and the Properties of the Resultant

WEN-YEN CHIANG and CHUN-MIN HU, *Department of Chemical Engineering, Tatung Institute of Technology, 40 Chungshan North Road, Sec. 3, Taipei, Taiwan, Republic of China*

Synopsis

Graft copolymerization of maleic anhydride (MA) onto PVA was carried out both in the presence and absence of the initiator. In the former case, the resultant was a copolymer containing a carboxylic acid and a keto-olefinic side chain. Therefore, the reaction product, viscosity, gel content, and mechanical properties differed from the resultant of the latter, which was obtained by esterification of PVA by MA. Both resultants showed polyelectrolytes characteristics. The dependence of the grafting percentage on the concentration of the initiator, the concentration of the monomer, the reaction temperature, and the reaction medium was studied. Grafted copolymers after heat treatment showed remarkable mechanical strength in the wet state when compared with original PVA.

INTRODUCTION

Poly(vinyl alcohol) (PVA) is a membrane material well-known for its good film-forming ability and toughness. However, because of its high hydrophilicity, it usually has to be turned into a completely undissolved material with good mechanical properties when used as a stable material. The two most common ways are: the grafting copolymerization of hydrophobic monomers to PVA[1] and the use of hydroxyl groups of PVA for modification reactions.[2]

The purpose of this study is to use maleic anhydride (MA) as a monomer, which is used not only to react with PVA for esterification but also to graft it onto PVA to form side chains. After these reactions PVA will contain unsaturated double bonds and ion dissociable groups. So, crosslinking and ionic bonding easily occur, increasing the mechanical properties and water resistance as a result of the reaction of double bonds and ionic covalent bonds.

EXPERIMENTAL

Materials

PVA BF-17, a product of Chang Chun Petrochemical Co. Ltd., Taiwan, DP = 1700, degree of saponification of 98.5–99.2 mol %, and viscosity of 25–30 cps was used. Maleic anhydride (MA), succinic anhydride (SA), and DMSO of reagent grades were purchased from Wako Pure Chemical Industries Ltd. Potassium persulfate (KPS) of a reagent grade used as the

initiator was purchased from Kanto Chemical Co. Benzophenone (BP) and benzoin ethyl ether (BEE) of reagent grades were purchased from Tokyo Kasei. Solvents such as chloroform, methanol, and acetone were used without further purification.

Graft Copolymerization

All graft copolymerizations were carried out in a four-necked flask equipped with a magnetic stirrer, thermometer, condenser and nitrogen inlet. The general experimental procedure and an example were as follows: PVA 5 g and MA 5 g were dissolved in 95 g DMSO after being stirred in an atmosphere of nitrogen. The reaction temperature was adjusted as needed (such as 60°C), then 0.5 g of KPS was added as an initiator. The reaction lasted for 5 h. The reaction was stopped at the predetermined reaction time by adding a small amount of hydroquinone. The reaction mixture was concentrated to about 20% of its original volume at 60°C under a reduced pressure, and was then added to chloroform to precipitate the polymer.

Purification of Copolymer

The products precipitated from chloroform were a mixture of grafted copolymer, unreacted PVA and homopolymer of maleic anhydride. They were separated and purified as shown in Chart 1:

Polymer reaction mixture (10.0 g)

$CHCl_3$

Soluble part
(Unreacted MA 2.48 g)　　　　　Undissolved part (7.5 g)

Acetone

Undissolved part
(6.77 g)　　　　　　　Soluble part
(MA homopolymer 0.73 g)

CH_3OH

Undissolved part
(Unreacted PVA 0 g)　　　　Soluble part

Concentrated
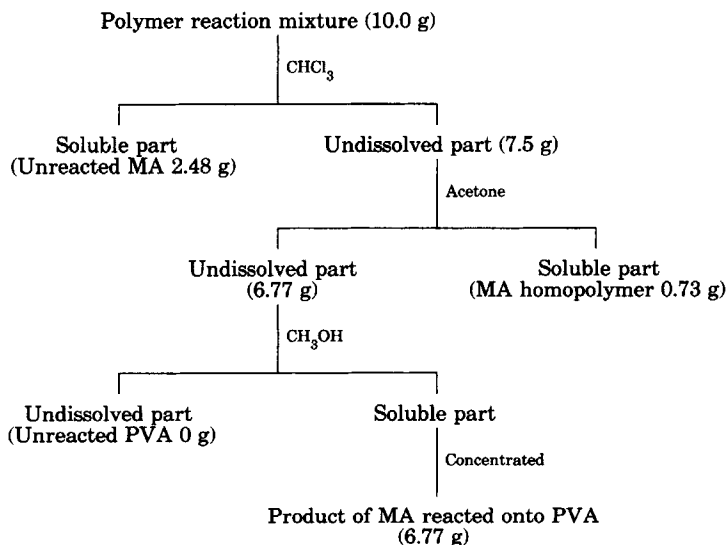
Product of MA reacted onto PVA
(6.77 g)

Chart 1. The Separation Procedure

If there is no need to know the weight of unreacted MA and MA homopolymer, the reacted mixture can directly be dissolved in acetone to eliminate the chloroform separation procedure.

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

$$\text{total conversion } (\%) = \frac{\text{wt of total MA polymerized}}{\text{wt of MA fed}} \times 100$$

$$\text{graft efficiency } (\%) = \frac{\text{wt of MA reacted onto PVA}}{\text{wt of total MA polymerized}} \times 100$$

$$\% \text{ of grafting} = \frac{\text{wt of MA reacted onto PVA}}{\text{wt of separated graft copolymer}} \times 100$$

$$\text{conversion } (\%) = \frac{\text{wt of MA reacted onto PVA}}{\text{wt of monomer fed}} \times 100$$

Preparation of Membrane of Graft Copolymer

The MA grafted PVA copolymer with high grafting percentage could be dissolved in distilled water as well as methanol, though that of low grafting percentage could be dissolved only in water. The membrane was formed by pouring the casting solution on a glass plate which was allowed to dry at 20–30°C in a vacuum to constant weight before the membrane was removed from the plate.

Heat, Chelating, and Irradiation Treatment of the Membranes

Heat Treatment

The films of water-dissolved graft copolymers were made by casting. Another approach was to have methanol-dissolved copolymers containing AIBN or BPO filmed. Then the films were treated in an oven at variously set temperature (100–150°C) and for various lengths of time (5 min–24 h).

Chelating Treatment

The graft copolymers were dissolved in distilled water. Then the solution was stirred when $CaCl_2$ or $ZnCl_2$ were added. Eventually membranes were formed by casting.

Irradiation Treatment

The graft copolymers were dissolved in methanol. The solution was stirred when either benzophenone (BP) or benzoin ethyl ether (BEE) was added. Membranes were then formed by casting. These membranes were irradiated by a high-pressure mercury lamp (manufactured by Ushio Electric Co., Model USH-500D) at a distance of 20 cm.

These treatments were as follows:
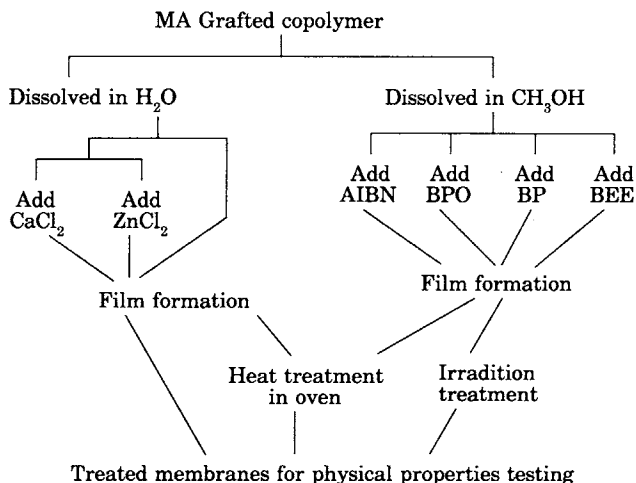
Measurement of Various Properties

Viscosity

The intrinsic viscosities of PVA and grafted copolymers were determined in distilled water as a solvent in an Ubbelohde viscometer at 30°C by extrapolating of η_{sp}/c to $c = 0$.

IR Spectra

IR Spectra were obtained from films or in admixture with KBr disk on a JASCO Model A-202 Spectrophotometer.

Gel Content

After heat and irradiation treatment the membranes of grafted copolymers were extracted by using hot water at boiling temperature for 24 h, and residual copolymers were dried and weighed. Gel content was calculated by the following equation:

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

Water Content

Membranes were first immersed in boiling water for 6 h and then taken out. The membranes were superficially dried with filter paper and weighed. Water content was calculated by the following equation:

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

Mechanical Properties

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

RESULTS AND DISCUSSION

The Reaction of PVA and Maleic Anhydride

In case PVA and maleic anhydride (MA) reacted in the absence or presence of the initiator potassium persulfate (KPS), the reaction products were separated by the procedure shown as Chart 1 in Experimental. After having dissolved the unreacted MA with chloroform, one could then extract the undissolved part with acetone. Here the reaction in the presence of KPS yielded an acetone soluble poly(maleic anhydride) (PMA) in black powder form, whose IR spectrum was similar to poly(maleic anhydride) reported.[3] The IR spectrum of the very part was also similar to those of PMA polymerized by the initiation of pyridine and KPS carried out in this research. The results are shown in Figure 1. However, the reaction in the absence of KPS did not yield the acetone-soluble part. In view of this fact, reaction mechanism and the product of the reaction of PVA and MA would, depending on whether there was a presence of an initiator or not.

Succinic anhydride (SA) has the same structure as MA except that the latter has an unsaturated double bond. Therefore, the reaction of SA to
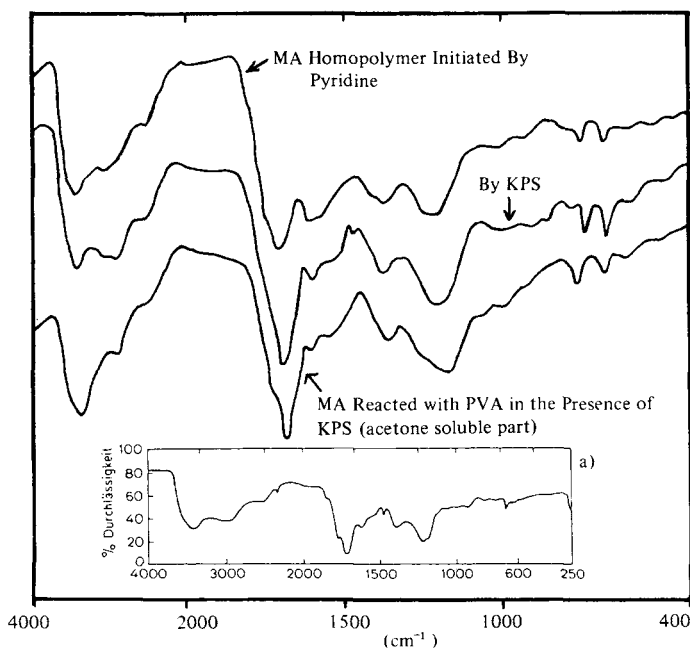

Fig. 1. IR Spectra of Poly(maleic anhydride) of MA Reacted with PVA in the Presence of KPS and Initiated By Various Initiators. a) IR Spectrum of PMA Reported By Braun[3].

PVA without an initiator implies that the graft copolymerization in PVA backbone is impossible; in fact, the product could be considered to be only an esterification of anhydride group of SA to OH in PVA.

In the same way, MA reacted easily to PVA in the absence of an initiator. The reaction confirmed that there took place only one esterification of anhydride group to OH group of PVA. The reaction conversion increased with the increase of the reactant concentration and reaction temperature. The IR spectra show the characteristic peaks of —COO— at 1720 cm^{-1} and —C=C— at 1640 cm^{-1}.

On the other hand, Ikada et al.[4] reported that KPS can abstract a proton from tertiary carbons of PVA to form a free radical on PVA main chain. Thus, with the presence of KPS in PVA system, two main reactions are considered to be occurring: one is the esterification in OH group and the other is grafting copolymerization in PVA main chain. In view of the bulky group of steric hindrance of anhydride group, it is difficult to consider the grafted side chain to be an anhydride polymer; it might be a cross-conjugated keto-olefinic structure that results from the rearrangement of maleic anhydride as reported by Bhadani and Prasad.[5] The proposed reaction mechanism and structure of the reacted PVA are shown as follows:

The rearrangement of maleic anhydride group in polymerization forms a ketoolefinic structure.

The proposed structure of the reaction of PVA and MA in the presence and absence of the initiator are shown as follows:

It is difficult to prove the suggested reaction mechanism from IR spectra from the reaction products, because the IR spectrum of the grafted PVA of proposed structure is similar to that of the product without initiator. However, conjugation of a carbonyl group with a conjugated C=C linkage will result in a lowering of the frequency.[6] In our case, the IR spectrum of the proposed structure obtained from the use of the initiator showed that the characteristic absorption peak was shifted to 1700 cm^{-1} as compared with 1720 cm^{-1} when no initiator was involved. This fact might corroborate the suggested structure of this research. The results of IR spectra are shown in Figures 2 and 3.

The Viscosities of the Reaction Products of PVA and MA

The measured viscosities of three kinds of polymers, namely, PVA, MA reacted onto PVA without initiator, and MA reacted onto PVA with initiator are shown in Figure 4. PVA solution shows a linear relationship between η_{sp}/c and c, and the calculated intrinsic viscosity is 0.88 according to the following equation[7]:

$$[\eta] = 66.6 \times 10^{-5} M_n^{0.64} \quad (30°C \text{ in } H_2O)$$

The calculated molecular weight is about 75,680, which is equal to the DP of 1720, a figure very close to the original PVA of 1700. However, the value of η_{sp}/c increases with the decrease of the concentration of copolymer obtained from the reaction of PVA and MA without an initiator. This reveals
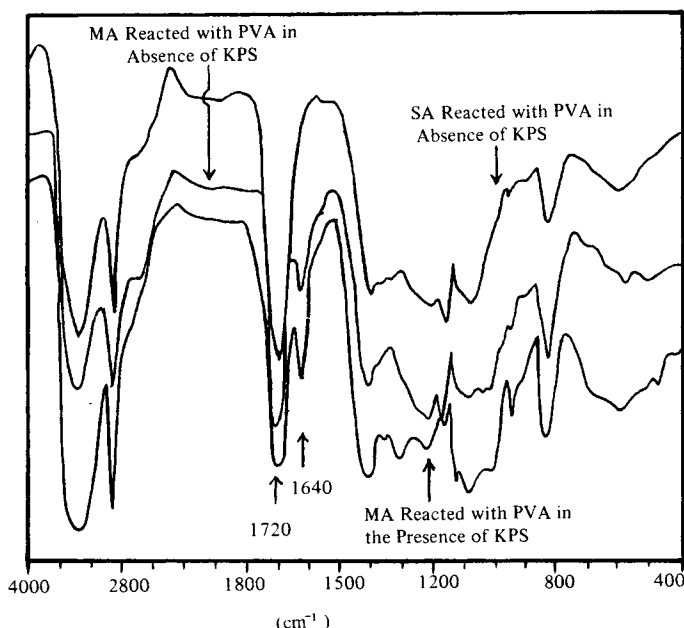

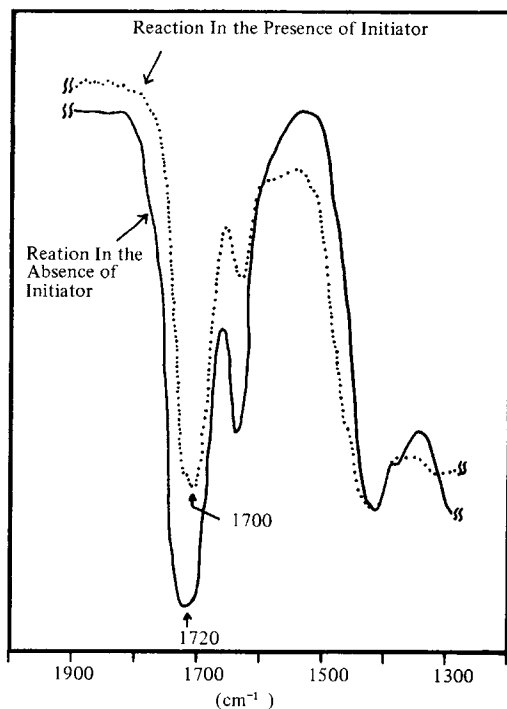Fig. 2. IR Spectra of Anhydrides (MA and SA) Reacted with PVA.

Fig. 3. Partial Infra-red Absorption Peaks of the Copolymers.

a characteristic of polyelectrolyte, a fact attributable to the many carboxylic acid groups contained in copolymer in PVA side chain. On the other hand, when the copolymer is obtained from the reaction of PVA and MA with an initiator at a high concentration (i.e., $c > 1$ g/dL), η_{sp}/c decreases with
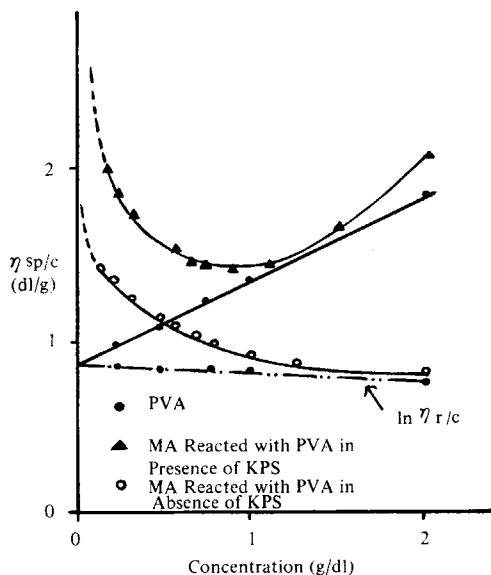

Fig. 4. Dependence of Polymer Solution Viscosity on Concentrations of MA Reacted with PVA.

the decrease of the polymer concentration in the same way as PVA solution does. However, when the polymer concentration is lower (i.e., $c < 1$ g/dL), η_{sp}/c increases with the decrease of the polymer concentration just like the polymer obtained from the reaction of PVA and MA without an initiator. This feature reveals the characteristic of polyelectrolyte. It is believed that in a high concentration of polymer solution a highly coiled shape is still maintained between polymer chains. However, in a dilute solution, polymer ions and low molecular counter ions are dissociated from the side chain of the carboxylic acid group in an aqueous solution. In a very diluted solution, H^+ ions are so far away from the polymer side chain that the segment has the same charges as to repulse each other, thus letting the polymer ion extend to a more unperturbed state and increase viscosity with the decrease of concentration. The proposed illustration is shown in the following:

Tight coil   Dissociation   Polymer ion
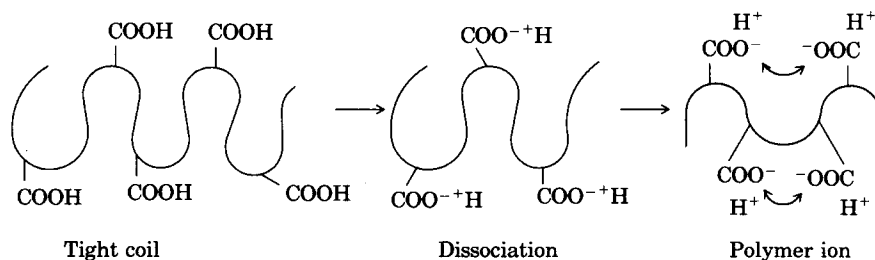
The viscosity of polyelectrolyte should obey the Fuoss equation[8] shown below:

$$\eta_{sp}/c = A/(1 + B\sqrt{c})$$

where $A =$ the intrinsic viscosity and $B =$ the interaction of ions between polymer ionic pairs. A and B are determined from Figure 5 by using the Fuoss equation. The results are shown in Table I.

Intrinsic viscosity showed that MA reacted onto PVA with initiator is larger than MA reacted onto PVA without initiator which is in turn larger than PVA. This result reflects that MA reacting onto PVA with an initiator has a higher molecular weight, which comes from the graft copolymerization of MA to form a long keto-olefinic side chain. However, MA reacting onto PVA without an initiator is an esterification, and this reaction product is bulkier and more polar. This fact could influence the viscosity.

On the other hand, the parameter B shows that MA reacting onto PVA without an initiator is larger than MA reacting onto PVA with an initiator. The difference reveals that the former contains more carboxylic acid groups than the latter; therefore, its interaction between polymer ionic pairs is stronger than MA reacting onto PVA with an initiator. From the results mentioned above, it is clear that the copolymer obtained from the reaction of PVA and MA using an initiator has a larger molecular weight, which undoubtedly comes from graft copolymerization. Since the esterification occurs at the same time, the copolymer contains few carboxylic acid groups, thus revealing the polyelectrolyte properties at a low polymer solution concentration.
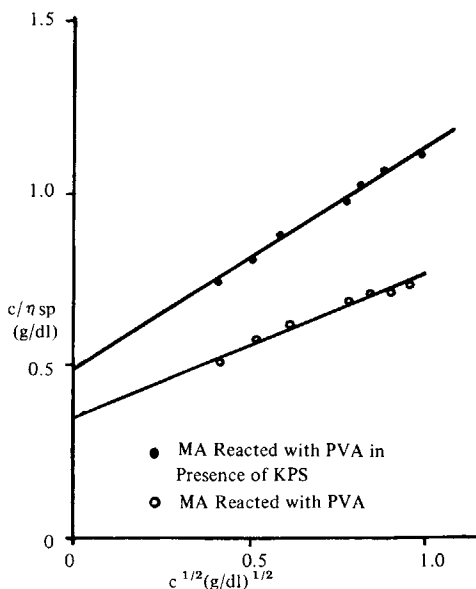
Fig. 5. Intrinsic Viscosities Determined By Using Fuoss Equation.

Mechanical Properties of Membranes

The mechanical properties of membranes after heat treatment in the dry state shows no difference between MA reacting onto PVA regardless of the presence or absence of an initiator; however, there is an obvious difference in case of the wet state as shown in Table II.

These differences may be attributed to the degrees of crosslinking. Because SA reacted onto PVA without an initiator, the resultant polymer has only SA added carboxylic acid group; therefore, the crosslinking can only occur between —COOH and —OH groups in the polymers. When MA reacted onto PVA without initiator, the resultant polymer even has only MA added carboxylic acid group as the additional side chain remains an unsaturated double bond, the crosslinking may be considered to occur on these double bonds, and the degree of crosslinking is larger than the above-mentioned polymer, thus showing higher mechanical properties. On the other hand, when MA reacted onto PVA with an initiator, the resultant polymer not only has the added MA groups containing carboxylic acid groups, but also has the grafted keto-olefinic groups. Thus MA grafted PVA

TABLE I
Constants A and B Determined by Fuoss Equation

	MA reacted onto PVA	
	Without initiator	With initiator
A^{-1} (g/dL)	0.48	0.36
$[\eta]$ (dL/g)	2.08	2.78
B/A	0.63	0.41
B	1.31	1.13

TABLE II
Mechanical Properties of Various Membranes

Membranes[a]	PVA (g)	DMSO (g)	MA (g)	KPS (g)	Temp (°C)	Time (h)	% of grafting[b]	Tensile strength (kg/mm²)		Elongation at break (%)		Water content (%)
								Dry state	Wet state	Dry state	Wet state	
PVA	—	—	—	—	—	—	0	7.4	0[c]	0	0	0
MA reacted onto PVA without KPS	10	95	8	0	100	5	25.8	6.2	0.3	0	18	45
	10	95	12	0	100	5	36.3	6.5	0.9	0	12	28
SA reacted onto PVA without KPS	10	95	10	0	100	5	28.9	5.5	0.3	5.2	7	15
MA reacted onto PVA with KPS	5	95	2	0.3	60	5	10.2	6.2	0.4	11	5	66
	5	95	5	0.3	60	5	26.1	6.0	1.0	0	15	30
	10	95	10	0.1	60	5	36.2	6.3	5.0	0	30	8
	5	95	10	0.3	60	5	51.4	7.2	6.3	0	35	6

[a] Membranes treated at 150°C for 10 h.
[b] Calculated by the equation shown in experimental.
[c] After heat treatment PVA membrane dissolved in water.

contained much more unsaturated double bond than MA reacting onto PVA without an initiator. Therefore, the crosslinking not only from the esterification but also from the unsaturated double bond might probably incur oxidation to form intercrosslinking. So the mechanical strength enhanced remarkably in the wet state. In connection with crosslinking, which was arrived at by heating in this study, it may be pointed out that photochemical crosslinking also brings about the formation of a cyclobutane ring as well as intercrosslinking.[9]

IR spectra of the membranes of SA and MA reacted onto PVA with and without an initiator show characteristic absorption peaks of OH group at 3350 cm^{-1} and —C=C— unsaturated double bond group at 1640 cm^{-1}. The peaks decrease with the increase of heat treatment time at 150°C. The former case suggested that crosslinking is brought about by the esterification of carboxylic acid group and hydroxy group while the latter case comes from the opening of double bond. The results are shown in Figure 6.

On the other hand, the gel content of membranes after heat treatment increases with the rise of the heat temperature. MA reacted onto PVA with an initiator shows higher crosslinking densities than the others, and it also improves the structure of MA reacted onto PVA. In addition, it has far more functionalities, the results are shown in Table III.

Appling UV irradiation curing to MA grafted PVA membrane for a period of 20 min to 2 h resulted in the highest gel content of 16% at the maximum, in contrast with 90% when heat treatment was adopted. Of the two pho-
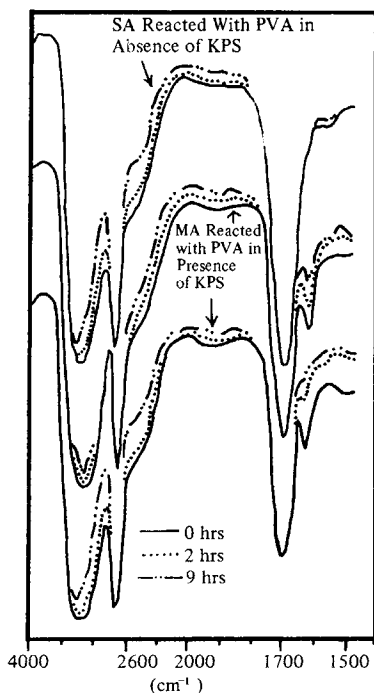

Fig. 6. Effects of the Heat Treatment Time and Temperature On the IR Spectra of PVA Membranes After Reaction With MA or SA.

TABLE III
Gel Content of Various Membranes at Various Heat Treatment Time and Temperature

Heat treatment time (min)	Gel content (%)			
	SA reacted onto PVA without KPS at 150°C	MA reacted onto PVA without KPS at 150°C	MA reacted onto PVA with KPS	
			At 150°C	At 100°C
0	0	0	0	0
5	8.5	71.2	76.5	10.4
30	37.5	78.1	81.2	33.8
60	68.0	82.3	85.7	51.3
240	85.4	89.6	92.4	61.3
1200	87.6	93.8	95.4	84.9

toinitiators used benzophenone was found to be better than benzoin ethyl ether (in gel content, the former being 16% while the later 12%). As a result, UV curing is found to be inferior to heat treatment in crosslinking. Thus further investigation became pointless. The addition of chelating agents such as zinc chloride and calcium chloride were found to exert no effect on the formation of the ionic bonding between the polymer chains, a reaction expected to increase the mechanical strength and water resistance of membranes.

The Factors Influencing the MA Reacted Onto PVA Graft Copolymerization

Reaction Temperature

When the reaction temperature ranges betwen 50 and 90°C, it appears that the temperature exerts no influence on total conversion, graft efficiency, percent grafting, and conversion; however, a higher reaction temperature has a faster reaction rate on account of the change in the reaction solution color. The results are shown in Figure 7.

Concentration of Initiator

Total conversion, conversion, and percentage of grafting increase with the increase of the concentration of an initiator; however, total conversion increases faster than conversion. Because homopolymer of maleic anhydride increases with the increase of initiator concentration. The results are shown in Figure 8.

Monomer Concentration

With increasing monomer concentration, there is a faster increase in the conversion than the total conversion; therefore, the graft efficiency increases with the increase of monomer concentration. The results are shown in Figure 9.
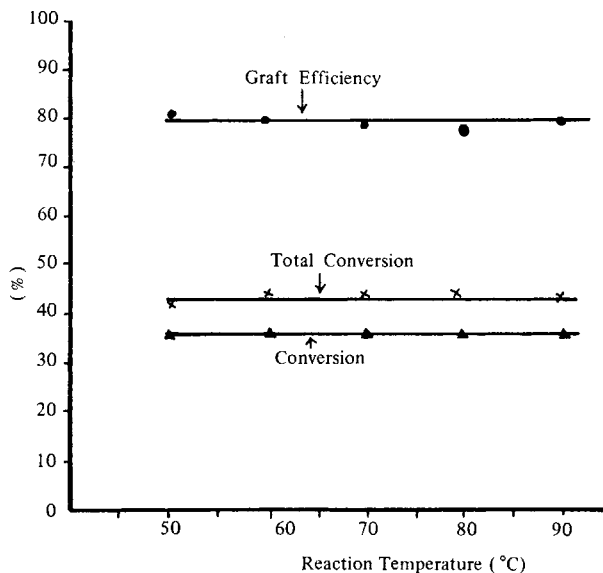
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Fig. 7. Effects of the Reaction Temperature On Graft Efficiency Total Conversion, and Conversion (PVA 5g, DMSO 95g, MA 5g, KPS 0.1g).

Reaction Medium

In an aqueous solution even with an initiator, MA does not react with PVA. It is attributed to the fact that MA in water will be converted into maleic acid, a very stable α, β-disubstituted monomer, which is difficult to react onto PVA at the reaction temperature between 60 and 90°C.[10] This was proved by the total absence of reaction of maleic acid with PVA in DMSO when an initiator is used.
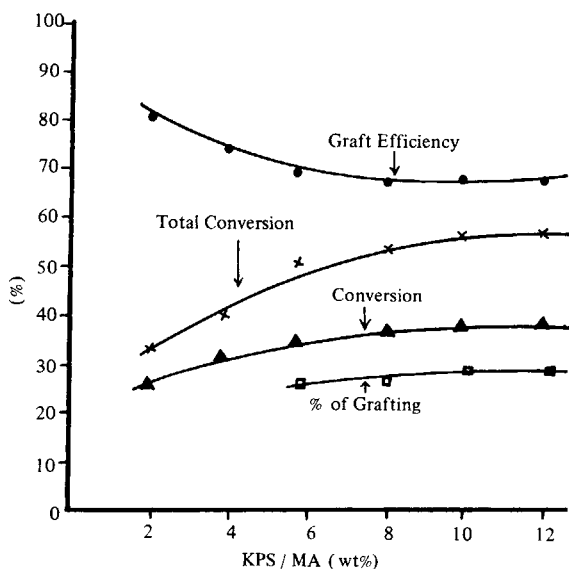
Fig. 8. Effects of the Concentration of the Initiator Efficiency, Total Conversion, Conversion and % of Grafting. (PVA 5g, DMSO 95g, MA 5g at 60°C).
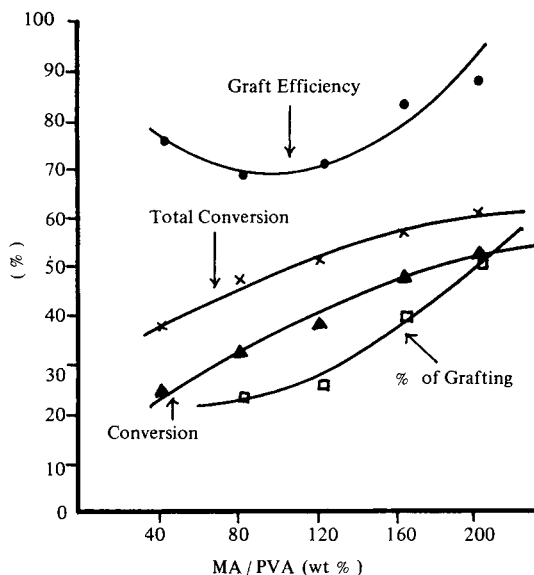
Fig. 9. Effects of the Concentration of Monomer On Graft Efficiency, Total Conversion, Conversion, and % of Grafting. (PVA 5g, DMSO 95g, KPS 0.3g at 60°C).

CONCLUSION

By the results of the products, viscosities, gel contents, and mechanical properties, the reaction of MA with PVA in DMSO without an initiator is an esterification; however, with initiator both esterification and grafting copolymerization will occur. Total conversion, graft efficiency, percent grafting, and conversion are independent of reaction temperature but are dependent on the concentration of initiator, monomer concentration, and reaction medium. A High percentage of grafting results in products of higher mechanical strength in the wet state after heat treatment.

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