

Studies on Graft Copolymerization of Glycidyl Methacrylate onto Poly(vinyl chloride) and Curing Behavior of Its Grafted Copolymer

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SYNOPSIS

Poly(vinyl chloride) was dehydrochlorinated in an alkali solution and then grafted with glycidyl methacrylate (GMA) using benzoyl peroxide as the free-radical initiator under a nitrogen atmosphere. The efficiency of grafting GMA under the influence of an alkali, GMA concentration, and duration of the grafting reaction, the viscosity properties, and the curing behavior with diamine were investigated. Maximum grafting to the extent of 46.4% was obtained. The optimum curing reaction conditions were investigated. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

The grafting copolymerization of vinyl monomers such as styrene and acrylates onto poly(vinyl chloride) (PVC) was extensively investigated.¹⁻²³ The graft methods that were commonly used are based on dehydrochlorination or γ -irradiation. For example, Mukherjee and Gupta and Al-Mobasher et al. investigated the dehydrochlorination of PVC in pyridine and then grafted it with styrene and 4-methacryloxy,2-2-hydroxybenzophenone using benzoyl peroxide (BPO), or azobisisobutyronitrile (AIBN) as the initiator.^{1,2} Sharma and Varma reported that PVC was grafted with styrene using $AlCl_3$ as the cationic catalyst in nitrobenzene.³ An increased number of active sites by dehydrochlorinating PVC in a sodium hydroxide solution and an increased extent of grafting using methyl methacrylate (MMA) as the comonomer were reported by Saroop et al.⁴ γ -Irradiation was also well developed.⁵⁻¹¹ Other PVC graftings were presented,¹²⁻²³ but monomers with a functional group grafted onto PVC were little studied. To investigate the grafting of func-

tional group monomers and the application of the grafted copolymer is therefore of interest.

In a previous article,²⁴ we investigated the grafting of hydroxyethyl methacrylate (HEMA) onto dehydrochlorinated PVC in a homogeneous procedure. The results of graft copolymerization of glycidyl methacrylate (GMA) onto dehydrochlorinated poly(vinyl chloride) (DHPVC) using benzoyl peroxide as a free-radical initiator to give a grafted copolymer containing the epoxide group are presented here. The effect of variations in reaction time, concentration of monomer, and dehydrochlorination at various concentrations of NaOH were investigated. Furthermore, the curing behavior of the grafted copolymer with diamine was also examined.

EXPERIMENTAL

Materials

PVC resins (S-70, $D_p = 1070$) was supplied by Formosa Plastic Co. GMA was distilled under reduced pressure. Benzoyl peroxide (BPO) was purified by dissolving in chloroform at room temperature and precipitating by the addition of methanol. Cyclohexanone and NaOH were used as received. Commercial methanol was distilled and used as the precipitant.

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Preparation of Dehydrochlorinated PVC⁴

A weighted quantity of PVC resin and 10 times the amount of NaOH aqueous solution in mass were fed into a round-bottom flask fitted with a reflux condenser. Dehydrochlorination proceeded for 2 h at 100°C. The dehydrochlorinated material in each case was washed with distilled water until all traces of alkali were removed and dried under vacuum at least 8 h. The reddish product is referred to as dehydrochlorinated PVC (DHPVC).

Graft Polymerization and Separation

DHPVC (5 g) and cyclohexanone (50 g) were left overnight for complete dissolution; the solution was then stirred and heated to 70°C in a nitrogen atmosphere. When the desired temperature was reached, the GMA monomer (a known amount [10.65 g] containing a known quantity of BPO [1.818 g]) was added with continuous stirring at 70°C. The reaction was carried out for a predetermined time (2.5 h). The mixture was then cooled and poured into excess well-stirred methanol. The precipitated polymer was filtered and washed several times with methanol, then dried to constant mass at 50°C under vacuum. The precipitate was a mixture of a grafted copolymer of PVC-*g*-GMA and poly(GMA). Poly(GMA) was removed by Soxhlet extraction with 1,4-dioxane as the solvent. The remaining solid PVC-*g*-GMA was dried under vacuum and weighed. The filtrate [a solution of poly(GMA) in dioxane] was concentrated by a rotary vacuum evaporator; the residue was precipitated with methanol. The recovered poly(GMA) was dried and weighed.

Estimation of Extent of Grafting and Grafting Efficiency

Gravimetry

The grafting parameters were estimated from the mass of the sample before and after grafting. The percentage of grafting and the grafting efficiency were calculated according to the following relationships:

GMA % grafting

$$= \frac{\text{mass of grafted poly(GMA)}}{\text{mass of grafted copolymer}} \times 100\%$$

Grafting efficiency

$$= \frac{\text{mass of poly(GMA) in graft}}{(\text{mass of poly(GMA) in graft} + \text{mass of poly(GMA) homopolymer})} \times 100\%$$

Chlorine Estimation

The analysis of the chlorine content (percent by mass) of the sample was done with an elemental analyzer (Tacussel Coulomax 78) with 1-chloro-2,4-dinitrobenzene as the standard. The fraction of content of various grafted copolymers was calculated. The mass fraction of poly(GMA) in the grafted copolymers was determined by gravimetry; a linear calibration curve was obtained by plotting the chlorine content vs. the mass fraction of GMA grafted onto DHPVC (see Fig. 1). Hence, the percentage of grafting and chlorine content were converted to one another according to this calibration curve.

Viscometric Measurement

Viscometric measurements were carried out on solutions in the solvent tetrahydrofuran (THF) with an Ubbelohde viscometer at $30.00 \pm 0.05^\circ\text{C}$.

Gel Permeation Chromatography (GPC)

The molecular weight distribution of PVC and DHPVC was measured using a Shimadzu Model LC-6A gel permeation chromatograph equipped with an RI detector (Shimadzu, RDI-6A). The GPC measurement was performed in a polymer/THF solution (about 5–7 mg/10 mL) by means of two Styragel columns, i.e., G2000H and G3000H under the flow rate 1.0 mL/min at 40°C. The average molecular weight was calculated based on polystyrene standards.

Determination of Epoxide Equivalent for Grafted Copolymers²⁵

An accurately weighed sample of PVC-*g*-GMA (2–3 mg epoxide equivalent) was placed into a three-neck round-bottom flask (100 mL) fitted with a reflux condenser. Another flask as a blank test was concurrently prepared. A hydrochloride/pyridine solution (25 mL, 0.2*N*) was pipetted into each flask with swirling of the solution and gently heating until all the sample dissolved. Then, the solution was refluxed and stirred for 25 min. After refluxing and

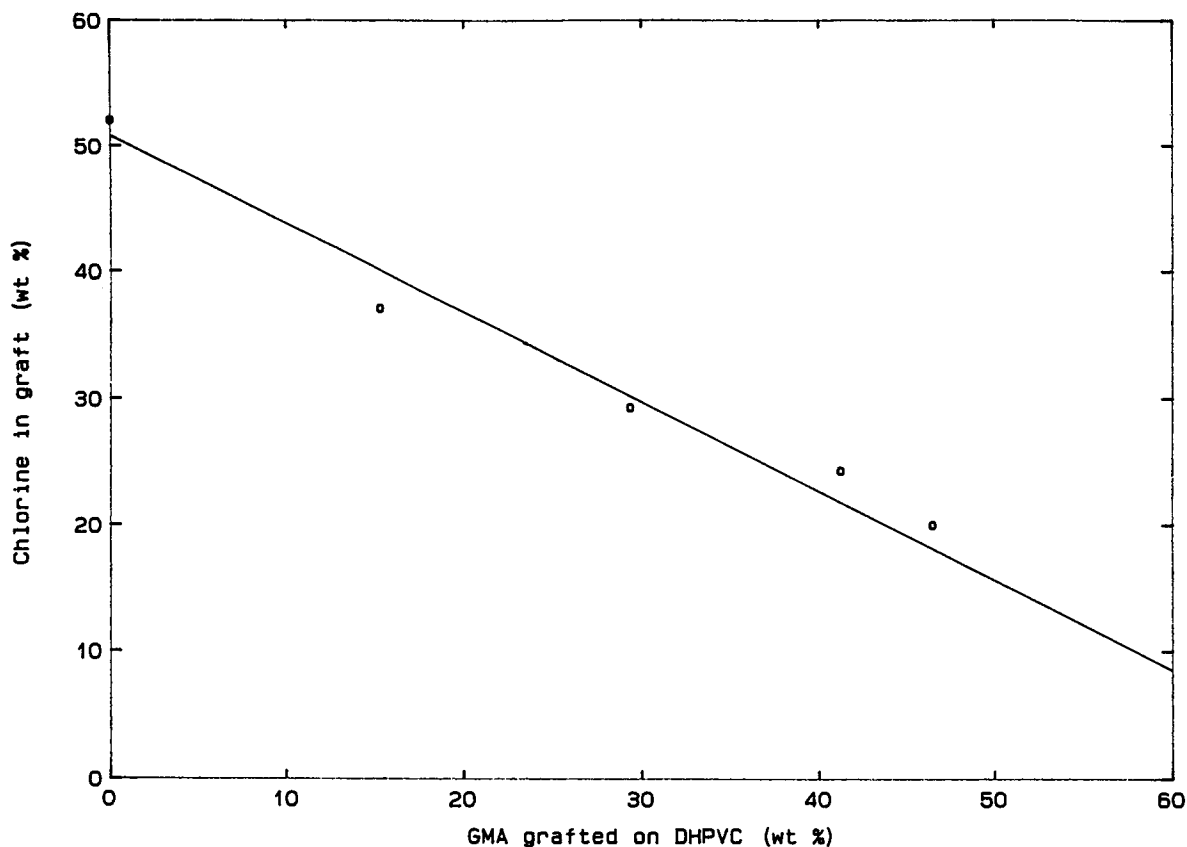


Figure 1 The relationship between fraction of grafting and content of chlorine.

cooling of the solution, methanol (30 mL) was added through the condenser to wash down adsorbed drops; phenolphthalein (15 drops) was added as an indicator and titration with NaOH/methanol (0.2*N*) solution required about 25 mL to reach the pink endpoint.

$$\text{Epoxide equivalent} = \frac{16 \times \text{sample weight}}{\Delta \times 0.2 \times 0.016}$$

in which Δ = the difference of titrant (mL) used between sample and blank.

Curing Reaction of Grafted Copolymer and Separation

The grafted copolymer (2.0 g) was dissolved in *N,N'*-dimethylacetamide (DMAc, 10 mL). An equivalent curing agent diamine (4,4'-diamino diphenyl ether) of which the quantity was taken according to the epoxide equivalent of PVC-*g*-GMA was weighed

and added to the solution. After it dissolved, the solution was poured into a Petri dish and placed in an oven that had reached the reaction temperature. The cured film was then subjected to Soxhlet extraction with THF as the solvent to remove the uncured part. After extraction, the residual solid was dried and weighed:

Curing efficiency

$$= \frac{\text{mass of residue after extraction}}{\text{mass of cured film before extraction}} \times 100\%$$

Characterization Techniques

IR spectra of solvent-cast films were measured on the spectrophotometer (Jasco FT/IR-7000) in the range 400–4600 cm^{-1} . DSC was carried out on a differential scanning calorimeter (DuPont Instruments 9900), at a heating rate 10°C/min in the range 20–160°C.

RESULTS AND DISCUSSION

Characterization of Graft Copolymer

IR spectroscopy is a well-known method to identify functional groups and to make quantitative analysis. The IR spectra of PVC, poly(GMA), and the graft copolymer are exhibited in Figure 2. The appearance of a new peak in the grafted sample at 1734 cm^{-1} indicates the addition of the carbonyl group of GMA. The graft copolymer also showed absorption at 909 cm^{-1} , attributed to the oxirane group in poly(GMA). The transmittance corresponding to the intensity ratio of $\nu_{\text{C=O}}(1734\text{ cm}^{-1})/\nu_{\text{C-Cl}}(636\text{ cm}^{-1})$ was calculated by the shoulder method and then a quantitative assessment was made to establish a relationship between the intensity ratio and percentage of grafting. The result is shown in Figure 3. The percentage of grafting of the GMA grafted onto PVC increased linearly with increasing intensity ratio.

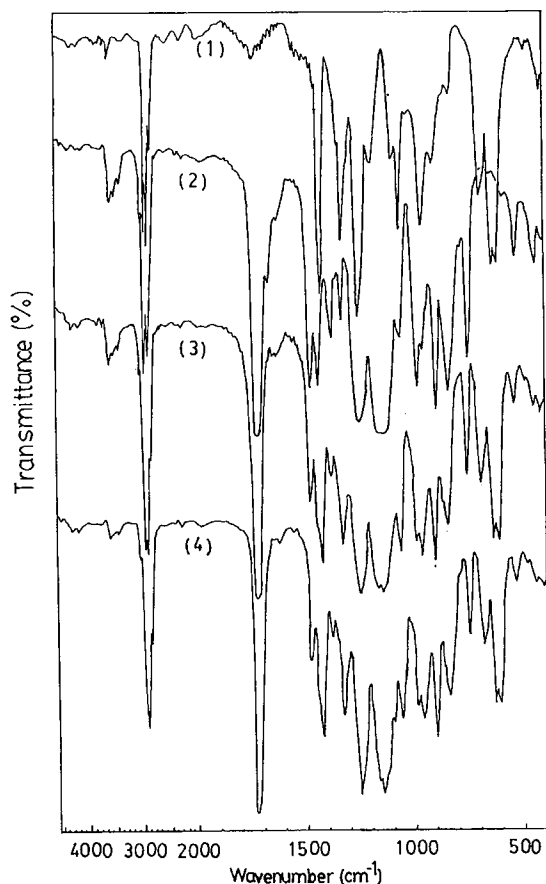


Figure 2 IR spectra of PVC, poly(GMA), and various fractions of grafted PVC-*g*-GMA: (1) PVC; (2) poly(GMA); (3) 15.2% grafted; (4) 29.3% grafted.

Table I Glass Transition Temperature of PVC, Various Fractions of Grafting PVC-*g*-GMA, and Poly (GMA)

Sample	Grafting (%)	T_g (K) (by DSC)	T_g (K) (by Fox eq.)
PVC	—	354.9	—
PVC- <i>g</i> -GMA	15.2	350.0	351.3
PVC- <i>g</i> -GMA	29.3	347.9	347.9
PVC- <i>g</i> -GMA	41.2	346.2	345.1
PVC- <i>g</i> -GMA	46.4	342.7	344.0
Poly (GMA)	—	332.2	—

Glass Transition Temperature (T_g)

The glass transition temperature (T_g) of unreacted PVC, various grafted PVC-*g*-GMA, and poly(GMA) are demonstrated in Table I. The T_g of poly(GMA) was almost 23°C smaller than that of PVC and the grafted copolymers had decreased T_g with increased percentage of GMA grafting. The values (according to the Fox equation:

$$\frac{1}{T_g} = \frac{X_1}{T_{g1}} + \frac{X_2}{T_{g2}}$$

where X_i was the weight fraction) coincided with the T_g analyzed by DSC. The single value of T_g of each grafted copolymer provided the evidence for complete separation of the copolymer mixture, i.e., the material is a grafted product with chemical bonding, not a physical blend.

Effect of Degree of Dehydrochlorination by Various Alkali Concentrations on the Grafting

The effect of alkali concentration on GMA grafting was studied at 5, 10, and 15% by mass (Fig. 4). The percentage of grafting and the efficiency of grafting gradually increased with alkali concentration. Increased alkali concentration of dehydrochlorination provides more active sites in the PVC main chains. Therefore, the value of the percentage of grafting and the efficiency of grafting increased.

Effect of the GMA Monomer Concentration on the Grafting

The effect of the content of GMA monomer concentration on grafting was studied in the range $0.5\text{--}2.0 \times 10^{-2}\text{ mol/g}$ DHPVC. A continuous increased ratio GMA/DHPVC in the system is exhibited by the results in Figure 5, but the grafting efficiency

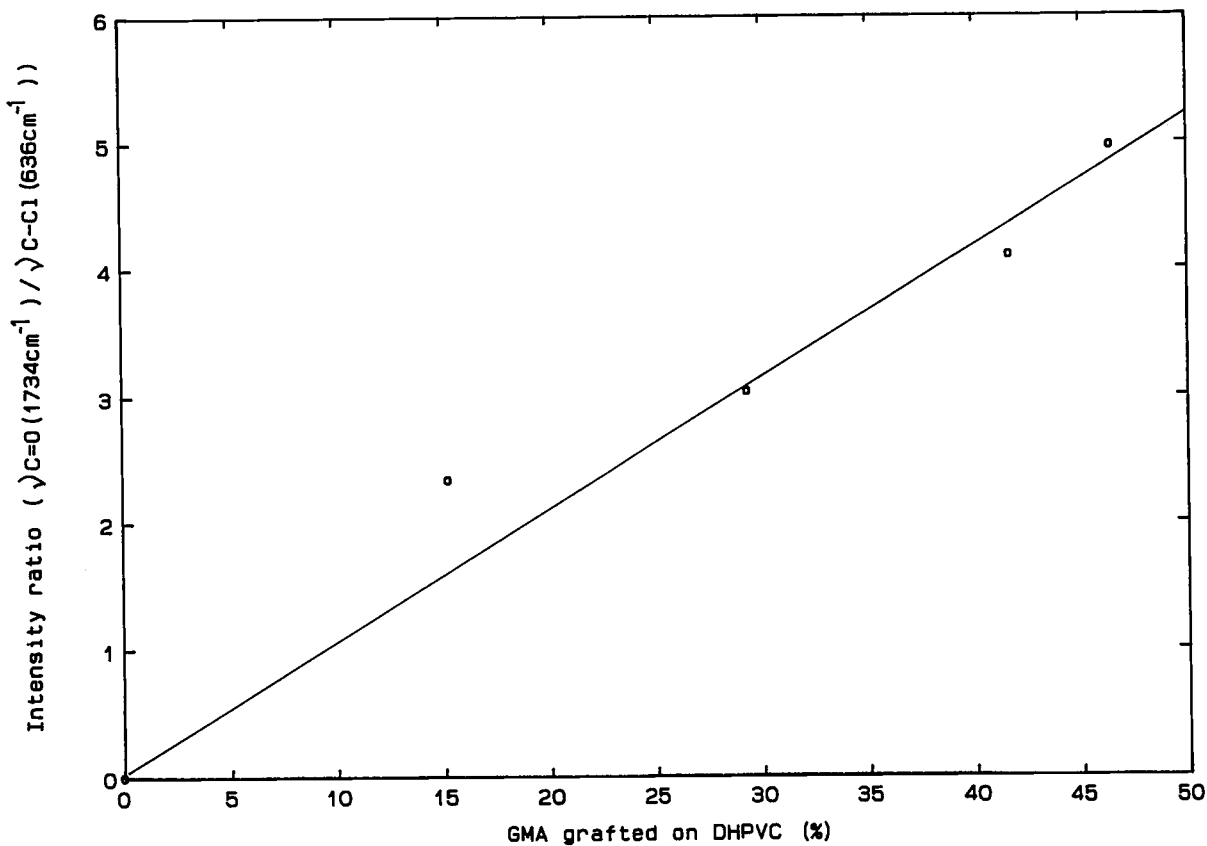


Figure 3 Fraction of grafting of GMA grafted onto PVC vs. intensity ratio $\nu_{C=O}(1734\text{ cm}^{-1})/\nu_{C-Cl}(636\text{ cm}^{-1})$ from IR spectra.

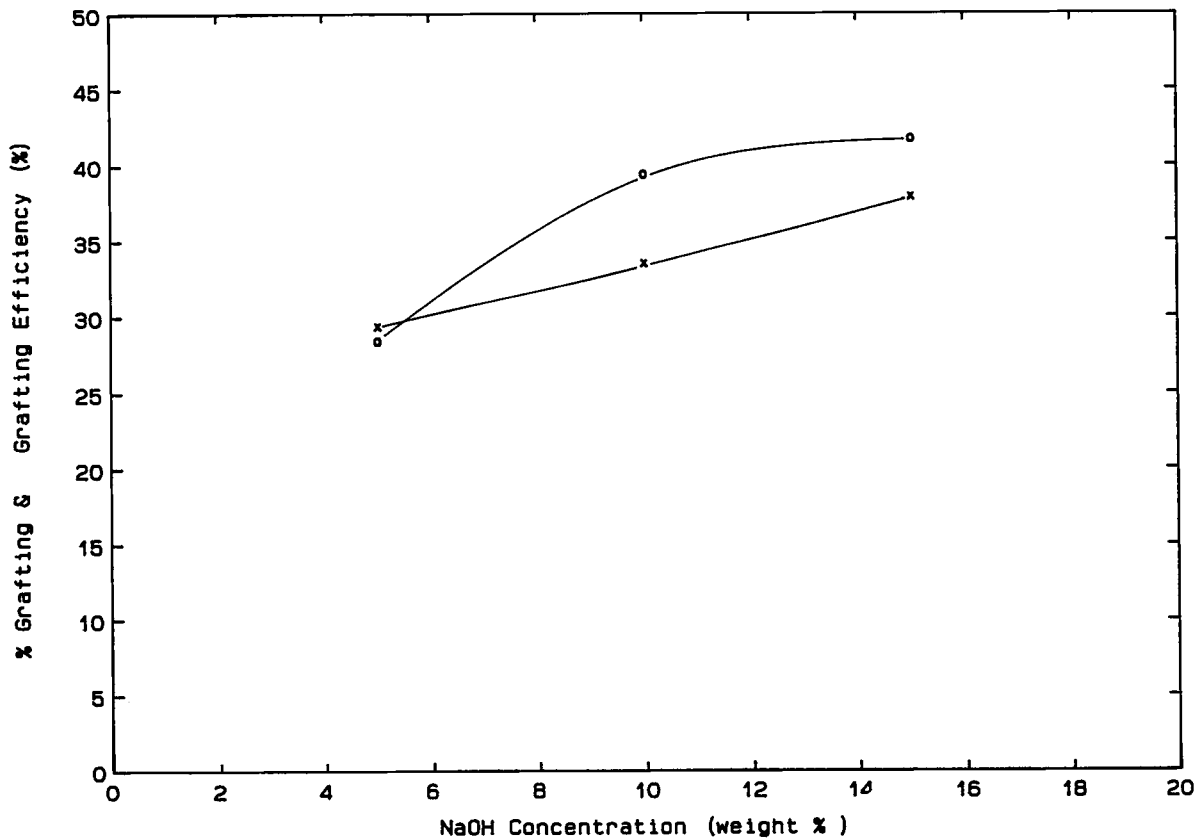


Figure 4 Effect of PVC dehydrochlorinated at various concentrations of NaOH in grafting reaction on fraction of grafting (x) and grafting efficiency (o).

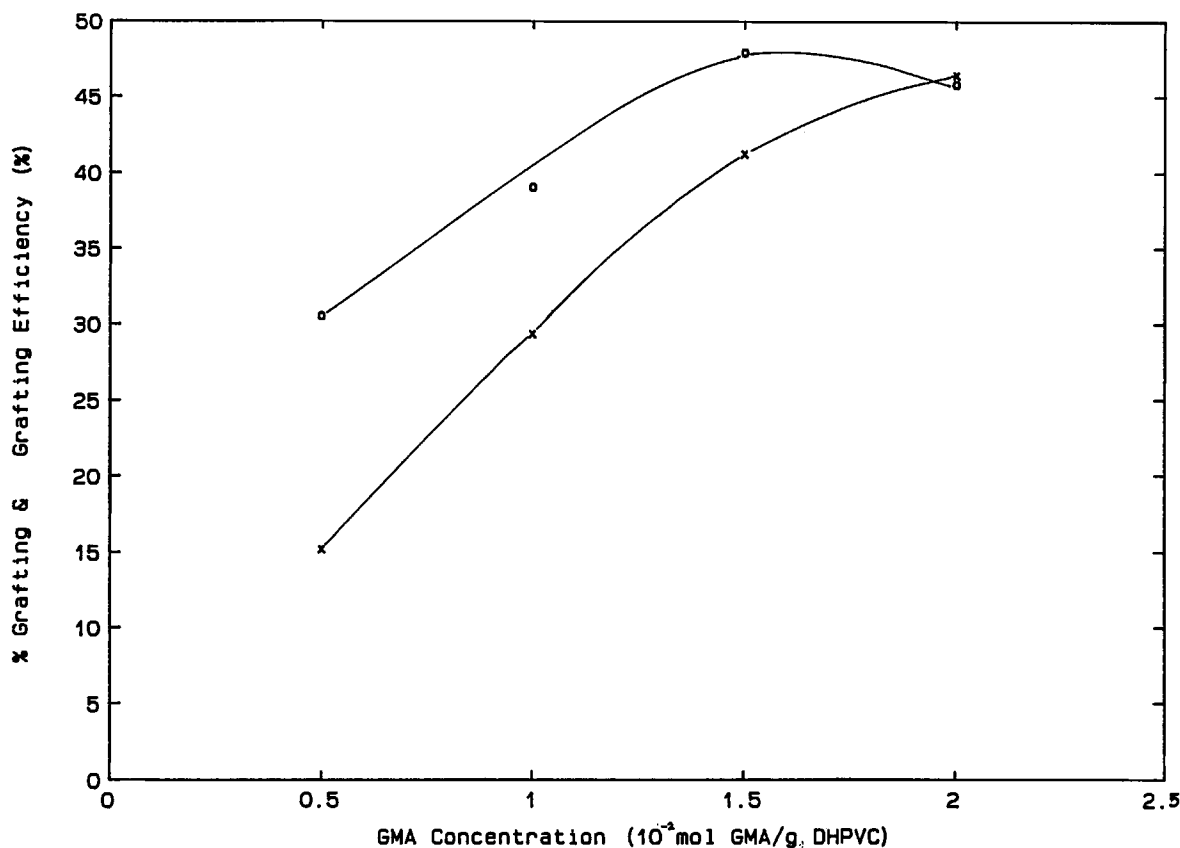


Figure 5 Effect of GMA concentration in grafting reaction on fraction of grafting (x) and grafting efficiency (o).

tends to a maximum at 1.5×10^{-2} mol/g DHPVC. This result is similar to that reported by Saroop et al.,⁴ meaning that the most reactive sites in DHPVC may be fully utilized by the GMA monomer at this concentration of 1.5×10^{-2} mol/g DHPVC. Above this amount, the excess GMA monomer generated a large amount of homopolymer, reducing the grafting efficiency. It also proved that homopolymerization was much more rapid than was the grafting of GMA onto PVC at a large concentration of GMA. The graft copolymerization is shown as Scheme 1.²⁴

Effect of Reaction Time

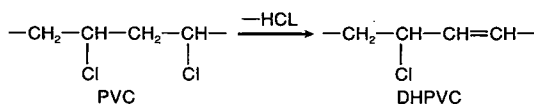
The effect of reaction time in the range 1–8 h on GMA grafting onto DHPVC is shown in Figure 6. The rate of GMA grafting increased continuously with increasing reaction time from 0 to 3 h. The percentage of grafting was 8.7% when the reaction period was 1 h. However, with increase to 3 h, the percentage of grafting reached a maximum value 29.2%. Beyond 3 h, there was shown a dramatic effect: The percentage of grafting and the efficiency

of grafting reduced with increasing reaction time. The grafted chains generally grow until the active sites are occupied completely and reach maximum grafting at the particular time. Subsequently, the grafting efficiency increases no more, but in this case, the grafted chains broke away from the PVC main chains when the period extended beyond 3 h.

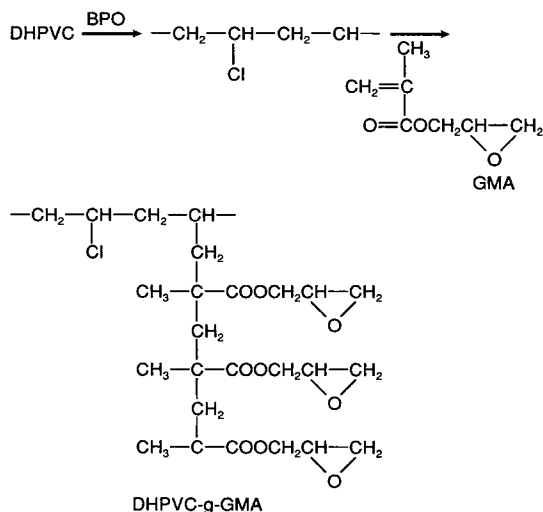
The duration of the reaction plays an important role for chain transfer. The attractions of the GMA monomer between the GMA homopolymer and the DHPVC main chain are different. Grafting onto the poly(GMA) chain is easier than onto DHPVC in all processes. During the period of 0–3 h, the numbers of GMA free radicals were many and the GMA homopolymer chains were short. The grafted chain grew with increasing time until the third hour. Then, two situations occurred: The active sites of DHPVC were reduced to almost nonexistence and the GMA homopolymer chains grew longer and resulted in the attraction to the GMA free radical being increased. If the grafted GMA side chains were encountered by a free radical, then they became broken from the side chain of the grafted PVC. The new free-radical

Scheme 1.

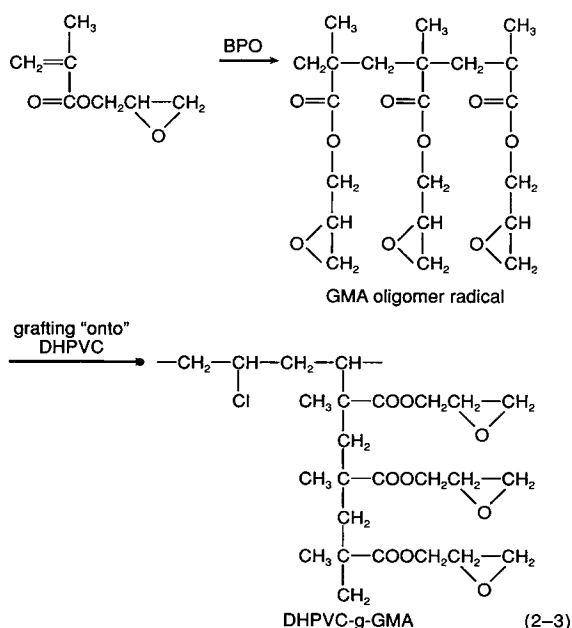
(I) PVC dehydrochlorination



(II) BPO radical initiator and GMA graft copolymerization



(III) GMA oligomer radical formation and grafting onto DHPVC



chains formed a GMA homopolymer during collisions with each other. Therefore, grafting decreased after 3 h, similarly to results reported by Sharma and Varma³ and Saroop et al.⁴

Intrinsic Viscosity

Intrinsic viscosities of PVC, DHPVC, poly(GMA), and various grafted copolymers were determined in THF solution at 30°C. The results (see Table II) demonstrated that the intrinsic viscosity decreased slightly for DHPVC relative to PVC. This occurrence is attributed to the PVC degradation under the dehydrochlorination in alkali aqueous solution. This can be proven by the GPC data. The weight-average molecular weight (\bar{M}_w) and number-average molecular weight (\bar{M}_n) of PVC and DHPVC measured by GPC are 1.5×10^5 and 6.9×10^4 and 1.2×10^5 and 6.1×10^4 , respectively.

The solubility parameters of PVC, poly(GMA), and THF are 9.20, 10.22,²⁶ and 9.52,²⁷ respectively. The compatibility of the PVC-THF system is therefore better than that of poly(GMA) in the THF solution. A linear relationship between grafting percentage and intrinsic viscosity shown in Figure 7 is obtained from the DHPVC ($[\eta] = 0.93$) to the pure poly(GMA) ($[\eta] = 0.24$). From this result, the intrinsic viscosities decreased with increasing fraction of grafting.

Curing Reaction of Grafted Copolymer with Diamine

Cross-linked PVC has been presented for some types in some patents,^{28,29} such as for PVC grafted by hydrolyzed silyl group monomers²⁸ and grafted PVC containing the hydroxyl and/or the carboxyl group crosslinked with those compounds containing an isocyanate group to form an abrasion-resistant urethane resin.²⁹ However, the cross-linking of the PVC-g-GMA has not been found in the literature; only found was the case in which the copolymer of vinyl chloride and 1-5% GMA was cross-linked through an organic silane that can be hydrolyzed.³⁰ Hence, the PVC-g-GMA copolymer cured with diamine is intended in this section. The investigations involved are the effect of various conditions on the curing efficiency, such as curing temperature, diamine equivalent, curing time, and percent grafting.

Effect of Curing Period

The effect of curing period on the diamine (4,4'-diamino diphenyl ether) curing reaction was investigated in the range 40-150 min. The reaction temperature was set at 100°C for various grafting copolymers (see Fig. 8). The curing reaction was complete after 90 min. Grafted PVC-g-GMA (29.3%) and 4,4'-diamino diphenyl ether were well mixed in

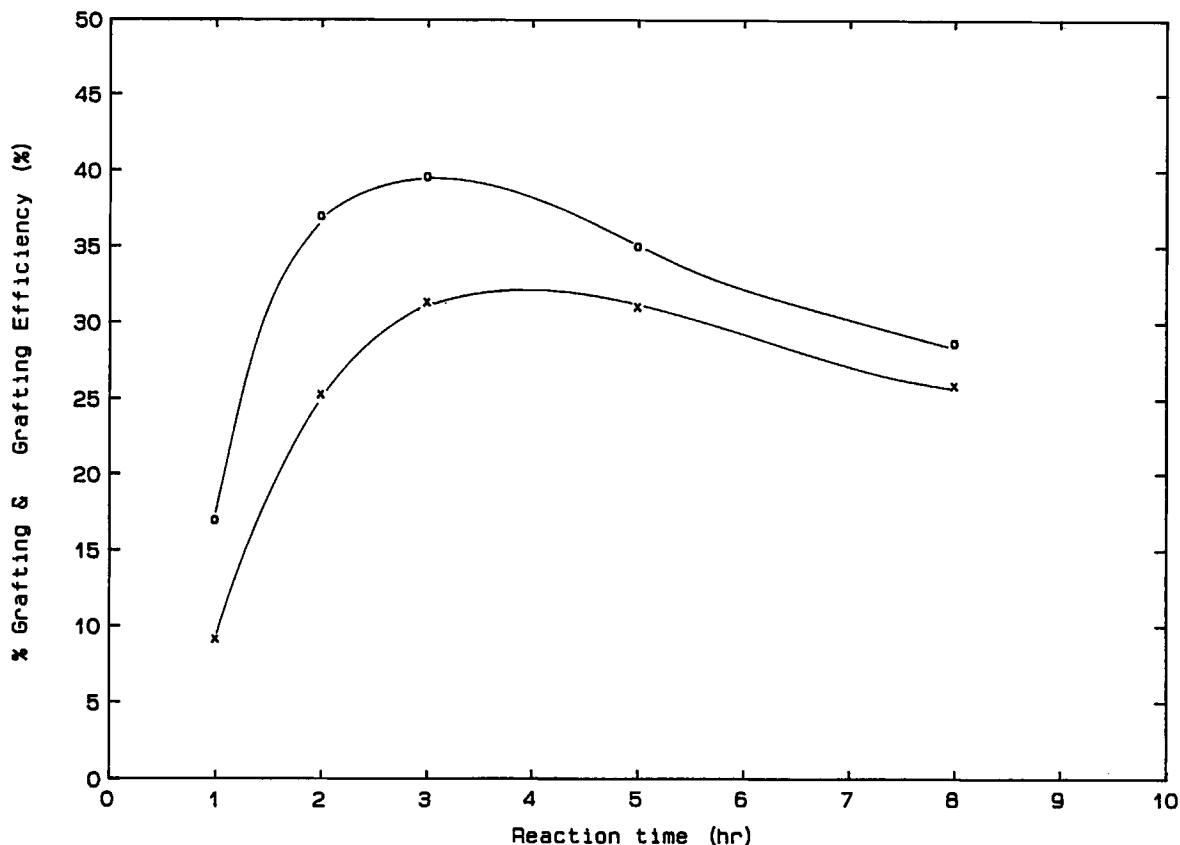


Figure 6 Effect of duration of grafting reaction on fraction of grafting (X) and grafting efficiency (O).

DMAc, then divided into several parts in Petri dishes and cured at 100°C. The cured film was analyzed by IR spectroscopy every 20 min from the curing time of 0 to 120 min. The transmittance corresponding to the ratio $\nu_{\text{C}-\text{C}(909\text{cm}^{-1})}/\nu_{\text{C}-\text{Cl}(636\text{cm}^{-1})}$

calculated by the shoulder method is shown in Figure 9. The oxirane group absorption was de-

Table II Intrinsic Viscosities of PVC, DHPVC, and Various PVC-*g*-GMA Samples in THF at 30°C

Sample	Grafting (%)	Intrinsic Viscosity (dL/g)
PVC	—	0.96
DHPVC	—	0.93
PVC- <i>g</i> -GMA	15.2	0.87
PVC- <i>g</i> -GMA	29.3	0.67
PVC- <i>g</i> -GMA	41.2	0.64
PVC- <i>g</i> -GMA	46.4	0.60
Poly(GMA)	—	0.24

creased when the curing period was increased. This result resembles that in Figure 8.

Effect of Diamine Concentration

The concentration of diamine (4,4'-diamino diphenyl ether) in the range of a 0.4–1.5 epoxide equivalent ratio is indicated in Figure 10. The curing efficiency was increased by the increasing diamine, almost four times between the small (0.4) and the large (1.5) concentrations of diamine, but there was little difference in the curing efficiency. This trend is explained by steric obstacles of PVC chains that became a barrier to the curing reaction. Although excess diamine was added, it could not make all oxirane groups react.

Effect of Curing Temperature

The curing reaction was carried out at four temperatures in the range 80–140°C (Fig. 11). Undoubtedly, the curing efficiency increased continuously with increasing reaction temperature. Raising the reac-

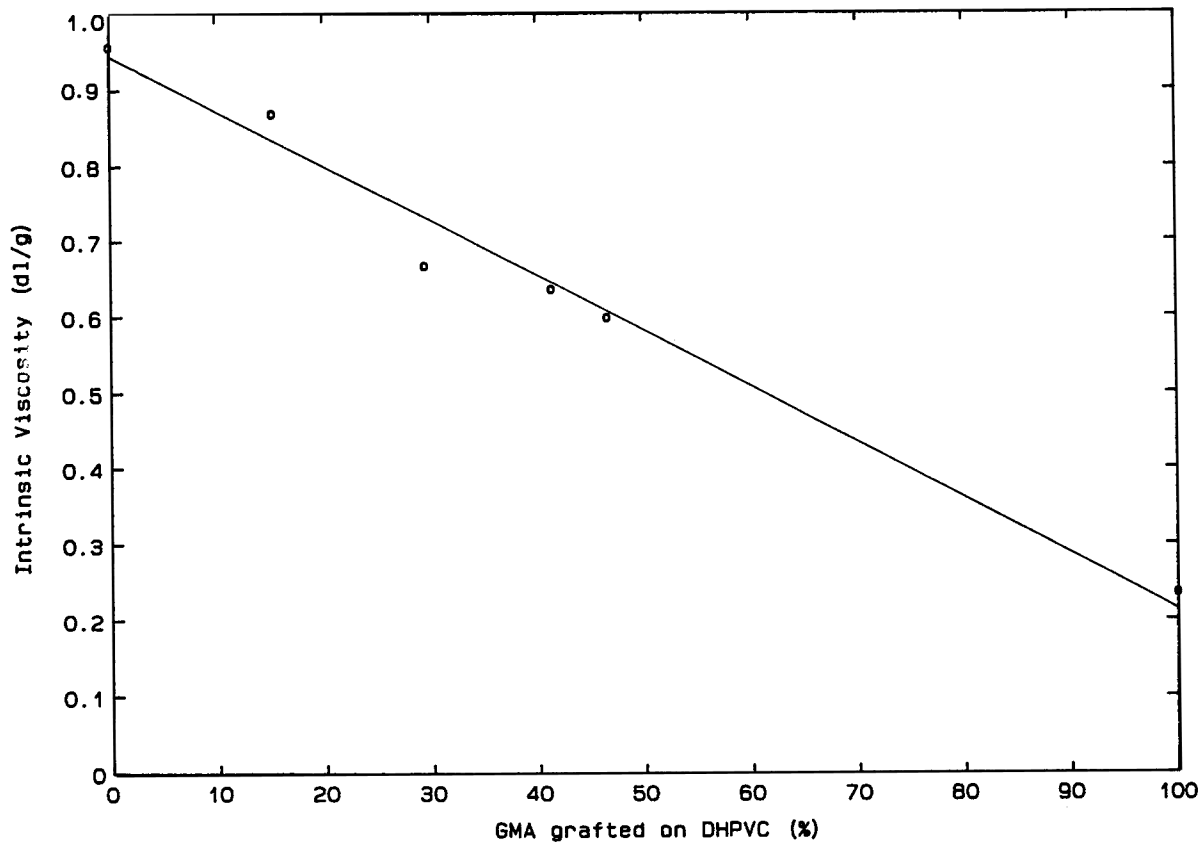


Figure 7 Intrinsic viscosities and GMA grafting degree.

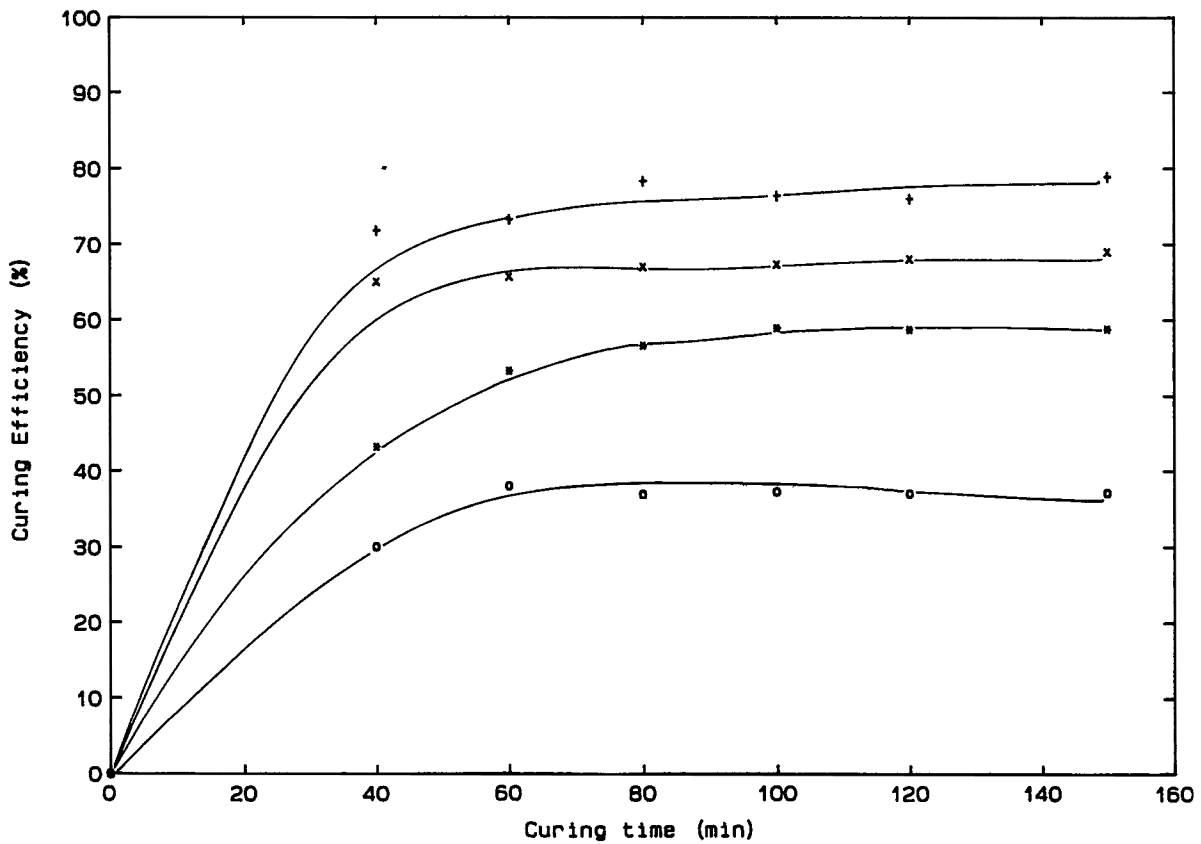


Figure 8 Effect of duration in curing reaction on fraction of curing efficiency: (O) 15.2% grafting PVC-g-GMA; (*) 29.3%; (X) 41.2%; (+) 46.4%.

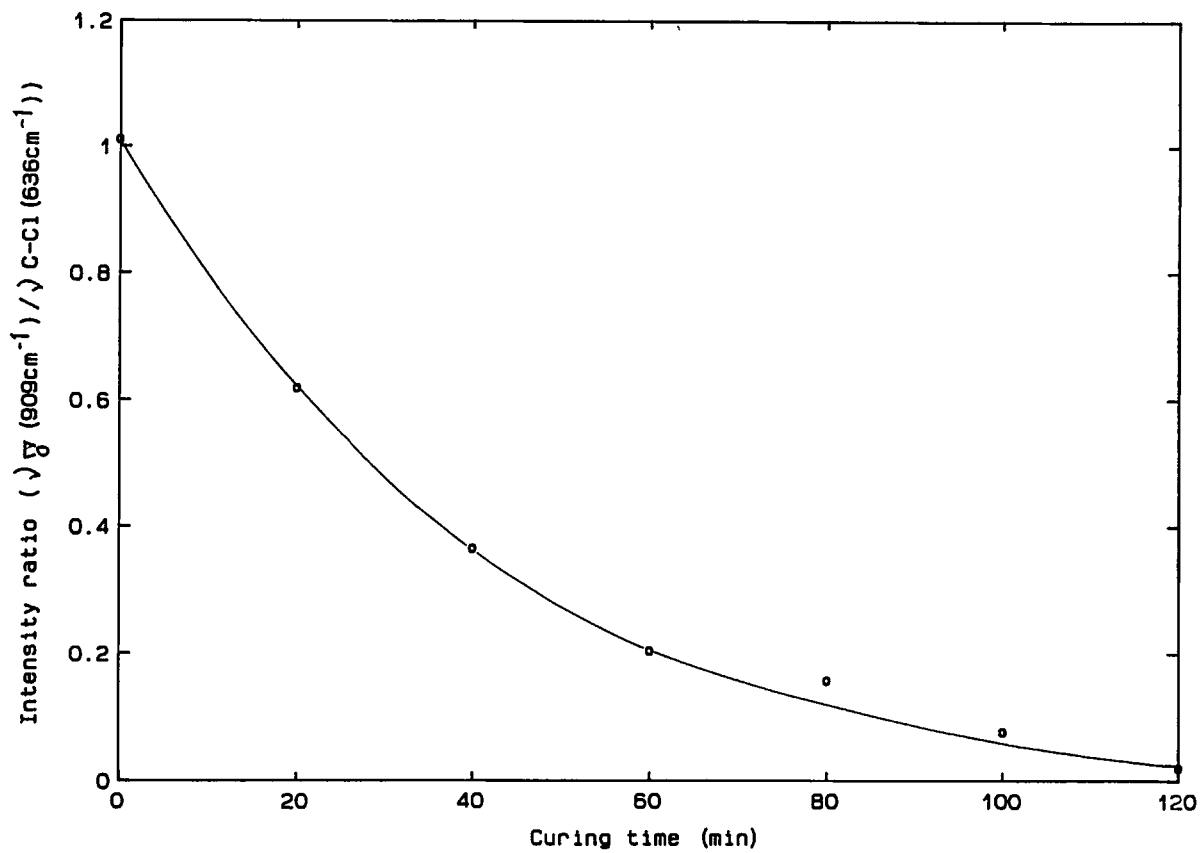


Figure 9 Relationship between IR spectral intensity ratio of the oxirane group and the curing period.

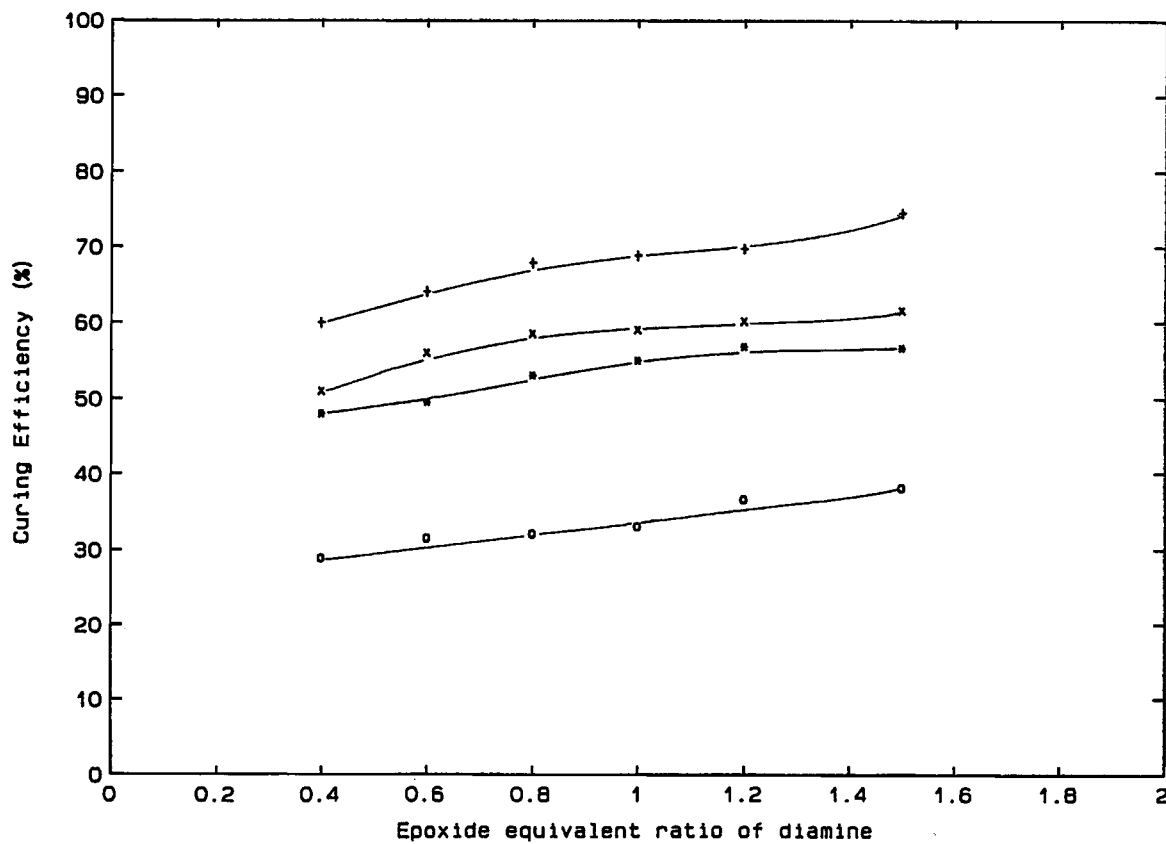


Figure 10 Effect of diamine concentration in the curing reaction on curing efficiency: (○) 15.2% grafting PVC-g-GMA; (*) 29.3%; (×) 41.2%; (+) 46.4%.

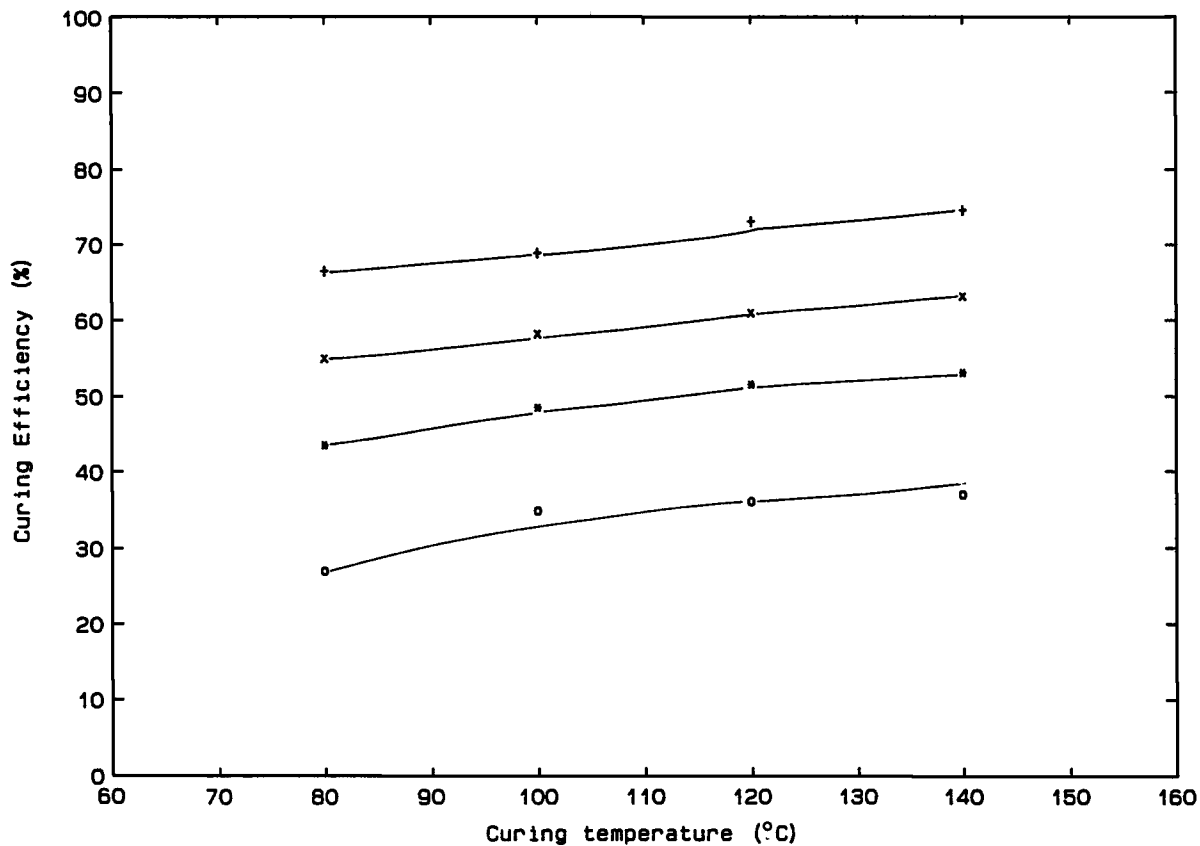


Figure 11 The effect of temperature in the curing reaction on the curing efficiency: (○) 15.2% grafting PVC-*g*-GMA; (*) 29.3%; (×) 41.2%; (+) 46.4%.

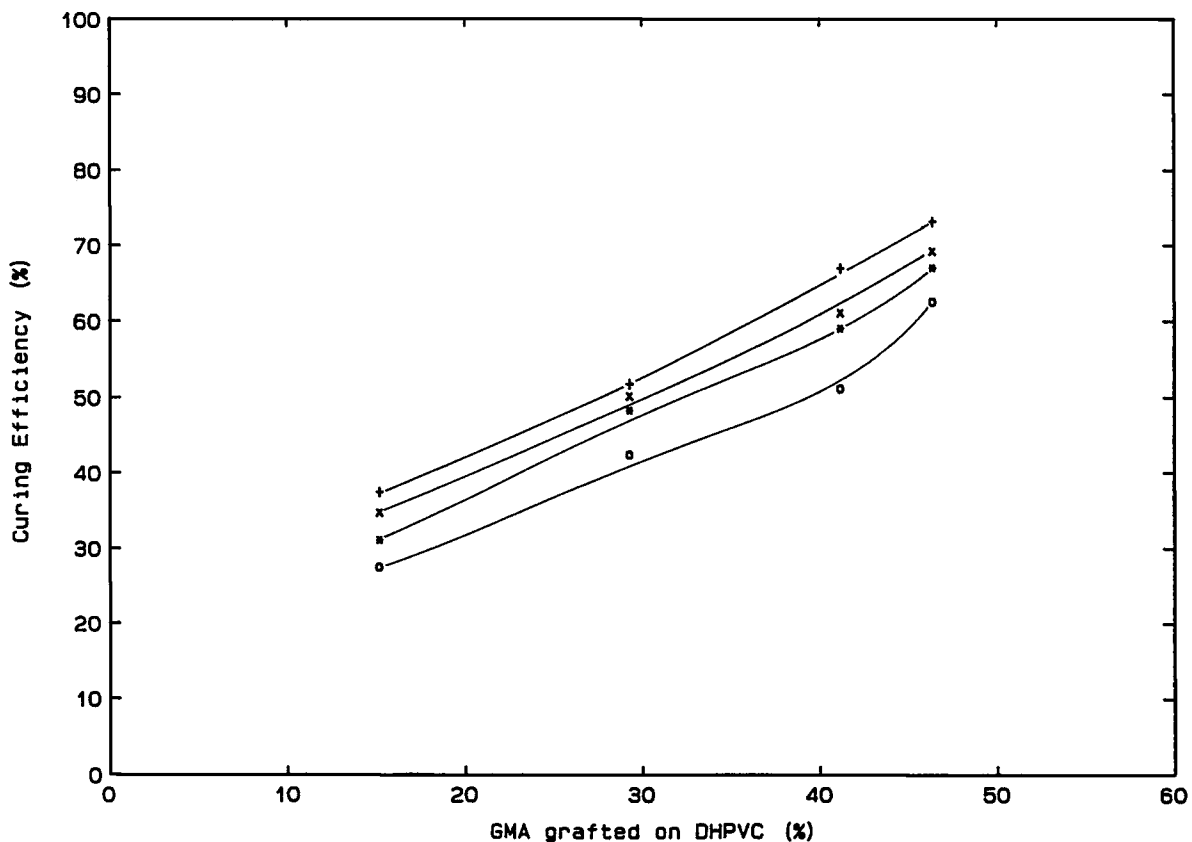


Figure 12 The effect of GMA fraction of grafting in curing reaction on curing efficiency: (○) 80°C; (*) 100°C; (×) 120°C; (+) 140°C.

tion temperature was a good method to increase the curing efficiency, but the cured films became brown at higher temperature (140°C). It seemed that the PVC main chains were damaged, so it is necessary to add an agent for thermal stability when curing at high temperature.

Effect of Percent Grafting

The effect of percent grafting of the grafted copolymer on the curing reaction was studied at 15.2, 29.3, 41.2, and 46.4% (Fig. 12). The curing efficiency increased with increasing fraction of GMA grafted onto DHPVC. The larger percentage of grafting copolymers had more oxirane groups, so that a polymer with more oxirane groups had a greater probability to cross-link with diamine. The four curves for various reaction temperatures showed an almost linear relationship.

CONCLUSIONS

The results show that grafting of GMA onto dehydrochlorinated PVC (DHPVC) by means of chemical initiation is easily performed. Various reaction conditions that affected the grafting copolymerization were investigated. An uncommon effect of reaction duration was discovered and the reaction period for optimum grafting was determined.

Curing of the grafted copolymer with diamine was carried out. The best curing conditions of duration, temperature, and diamine concentration were determined.

The grafted copolymer was not only cured with diamine but also enabled other applications. It can be the cross-linking material of the interpenetrating polymer network from PVC polyblends. Further research will be carried out on other uses of PVC-*g*-GMA.

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