

Mechanical Properties of Poly(vinyl chloride) Blends and Corresponding Graft Copolymers

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ABSTRACT: The mechanical properties of the poly(vinyl chloride) (PVC) and poly(glycidyl methacrylate) [poly(GMA)] blend system and the PVC and poly(hydroxyethyl methacrylate) [poly(HEMA)] blend system and their crosslinked films were investigated. At the same time, the mechanical properties for the corresponding graft copolymers such as PVC-*g*-GMA, PVC-*g*-HEMA, and their crosslinked films were also investigated in this study. The results showed that the tensile strengths for PVC-poly(GMA) blend systems were higher than those for PVC-*g*-GMA graft copolymer, and the tensile strengths for PVC-*g*-HEMA were higher than those for PVC-poly(HEMA) blend systems. However, the mechanical properties for the PVC-poly(GMA) blend system were not affected by the crosslinking of the blend system, but those for PVC-poly(HEMA) and their graft copolymers decreased with an increase of the equivalent ratio ($[NCO]/[OH]$) of the crosslinker. Finally, the surface hydrophilicity of the PVC-*g*-HEMA graft copolymer and PVC-poly(HEMA) blends were also assessed through measuring the contact angle. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* **67**: 307–319, 1998

Key words: mechanical properties; poly(vinyl chloride); graft copolymers; crosslinking

INTRODUCTION

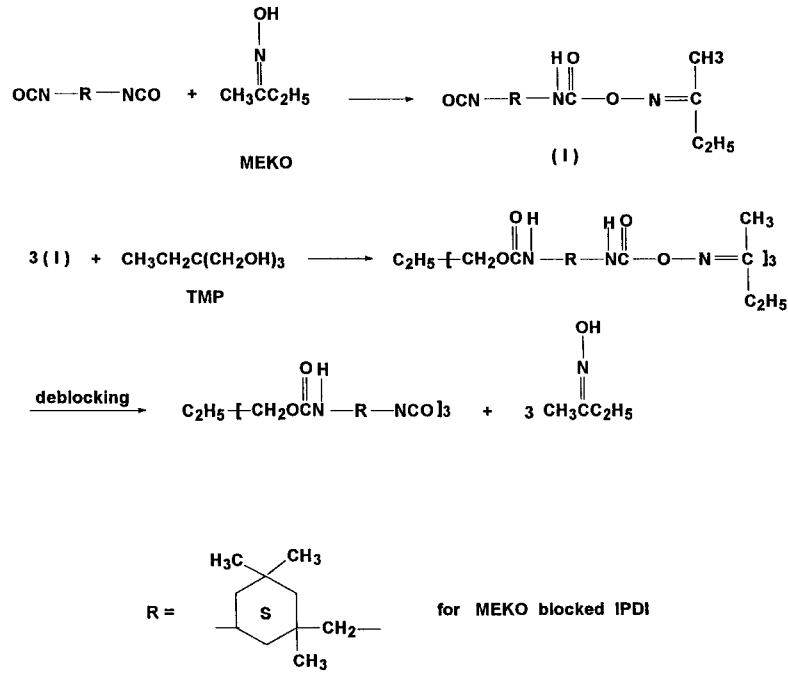
Polymer blends are physical mixtures of structurally different polymers that interact through secondary forces with no covalent bonding.¹ The importance of blending has increased recently because their superior properties over homopolymers can be compared to those of alloys over metals. The degree of compatibility usually determines the final properties of the blend. However, most polymer-polymer pairs are incompatible or have a low degree of compatibility.² The degree of compatibility, predicted by a viscometric method and thermodynamic principles, for poly(vinyl chloride)-poly(glycidyl methacrylate) [PVC-poly(GMA)] and PVC-poly(hydroxyethyl MA) [poly(HEMA)] blend systems were in-

vestigated in a previous study.³ The results showed that the compatible ranges for PVC-poly(GMA) and PVC-poly(HEMA) blend systems are located, respectively, at greater than 76 and 90% PVC. Hence, we investigated the mechanical properties for PVC-poly(GMA) polymer blends in compatible ranges containing various compositions. The mechanical properties of their curing films cured with diamine were also investigated. At the same time, the mechanical properties for PVC-poly(HEMA) polymer blends, in compatible ranges containing various compositions, and those of curing films cured with blocked diisocyanate (DI) were also investigated in this study.

However, to improve the compatibility of the polymer blend, many researchers in the past^{4–21} carried out the graft copolymerizations for PVC and vinyl monomers using dehydrochlorination or γ irradiation. For example, Krishnan and Krishnan,⁷ Goldberg and Vahiaoui,⁸ and Sigh et al.⁹ investigated the grafting of *N*-(vinyl pyrrolidine),

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Scheme 1 Synthesis of blocked diisocyanate TMP (MEKO-IPDI)₃.

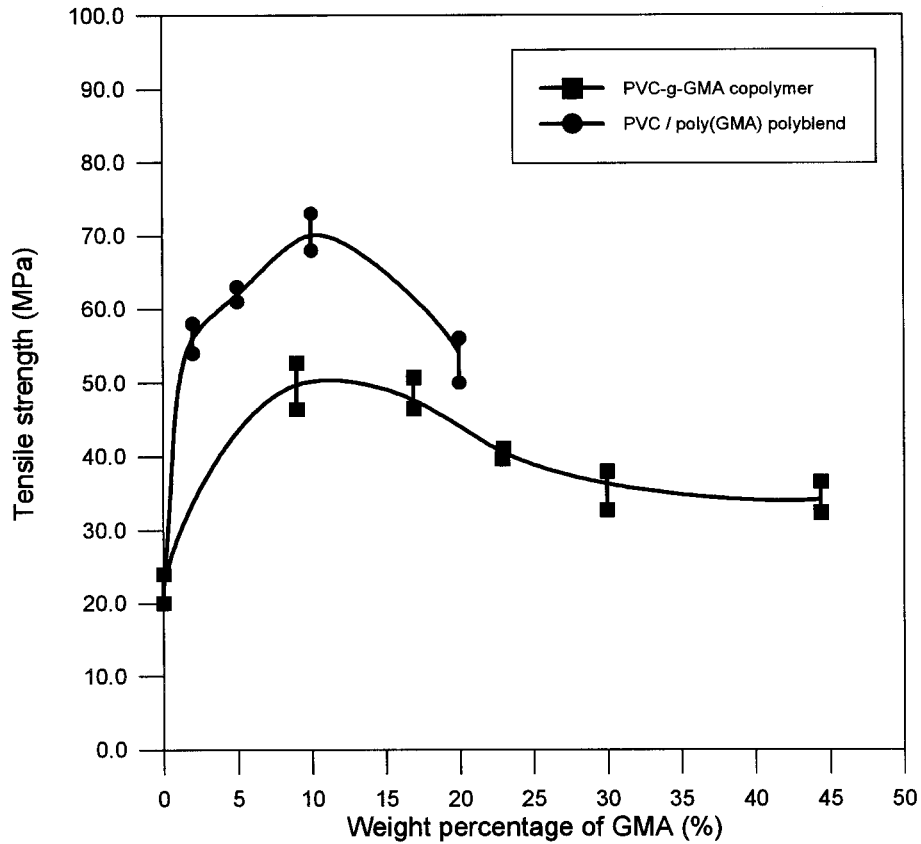


Figure 1 The comparison of tensile strength at various weight percentages of GMA between PVC-g-GMA and PVC-poly(GMA) blends.

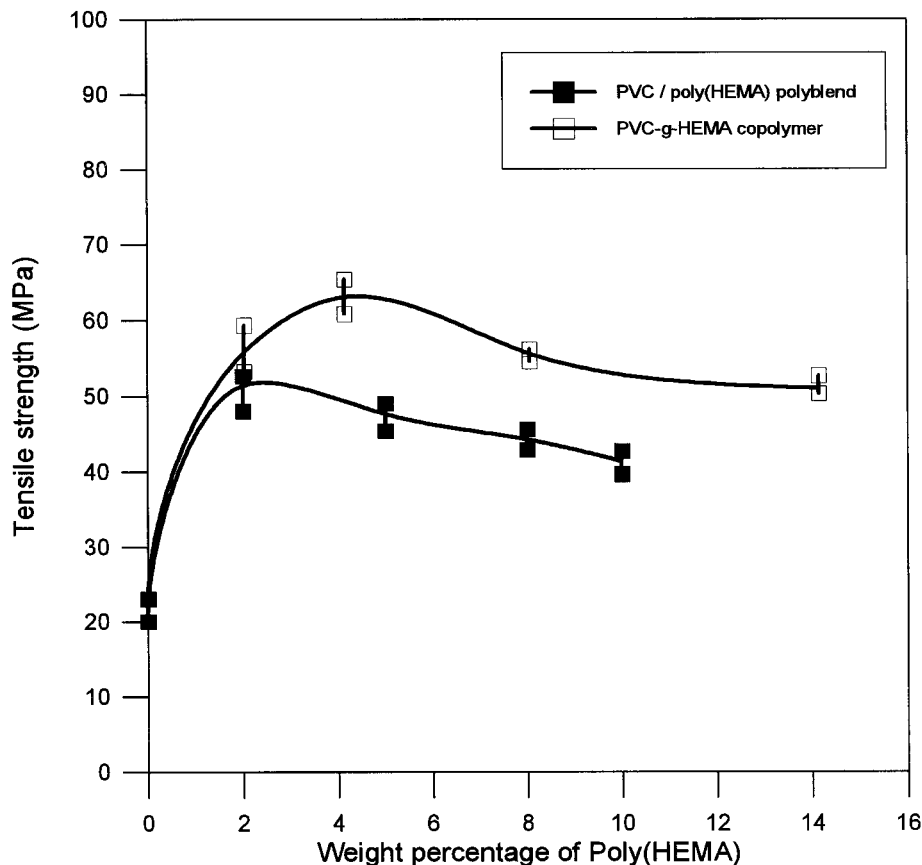


Figure 2 The comparison of tensile strength at various weight percentages of HEMA between PVC-*g*-HEMA and PVC-poly(HEMA) blends.

HEMA, and methacrylic acid grafted onto medical PVC sheets by UV or γ irradiation, respectively. Mukherjee and Gupta¹⁶ and Al-Mobasher et al.¹⁷ performed 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 initiator. The graft copolymers for PVC grafted with functional monomers (GMA and HEMA) using BPO as a free radical initiator under a nitrogen atmosphere were successfully prepared in previous reports.^{22,23} To compare the mechanical properties of these two blend systems with those of their corresponding graft copolymers, the PVC-*g*-GMA and PVC-*g*-HEMA graft copolymers were prepared, respectively, by the graft copolymerization of dehydrochlorinated PVC (DHPVC) with GMA and HEMA monomers. Furthermore, the mechanical properties of these two graft copolymers cured with diamine and blocked DI were also examined. In addition, the hydrophilicity of the

PVC-poly(HEMA) blends and PVC-*g*-HEMA grafts were also assessed.

EXPERIMENTAL

Materials

PVC resin (S-70; degree of polymerization = 1070) was supplied by Formosa Plastic Co. (Taiwan). HEMA and GMA monomer were distilled under reduced pressure. BPO was recrystallized by dissolving it in chloroform at room temperature and then precipitation by methanol. Trimethylolpropane (TMP, Hayashi Pure Chemicals), isophorone DI (IPDI, Tokyo Kashei Co. Ltd.), and methyl ethyl ketoxime (MEKO, Tokyo Kashei Co. Ltd.) were used to synthesize blocked DIs. 4,4'-Diaminodiphenyl ether (Fluka Co. Ltd.) was used as a crosslinker of PVC-*g*-GMA graft copolymers. *N,N*-Dimethyl acetamide (DMAc), acetone, cyclohexanone, and methanol were used as received.

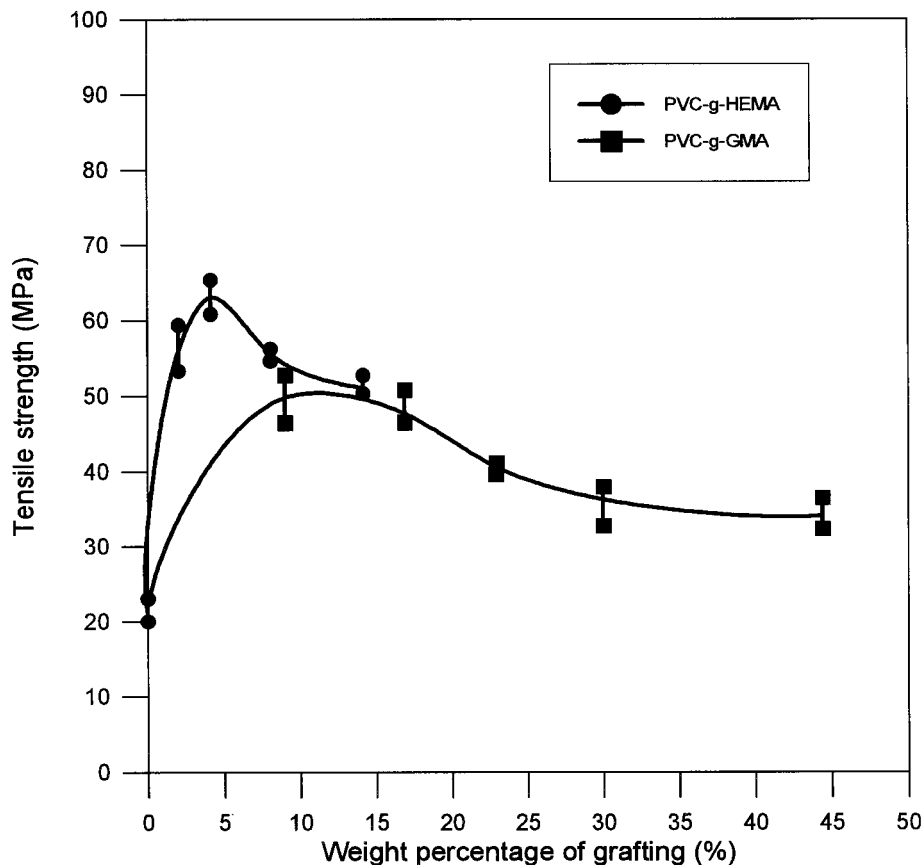


Figure 3 The change in tensile strength for PVC-g-GMA and PVC-g-HEMA graft copolymers with various degrees of grafting.

Preparation of PVC-g-GMA and PVC-g-HEMA Grafted Copolymer

Dehydrochlorination of PVC (DHPVC)

A weighed quantity of PVC resin and 10 times its amount of 10% NaOH solution by mass were fed into a round-bottom flask fitted with a reflux condenser.^{22,23} Dehydrochlorination proceeded for 2 h at 100°C. The dehydrochlorinated material in each case was washed with distilled water until removal of all traces of alkali and then dried under a vacuum for at least 8 h. The reddish product is referred to as DHPVC.

PVC-g-GMA Grafted Copolymerization and Separation

A typical graft copolymerization of DHPVC with GMA is as follows.²³ First DHPVC (5 g) and solvent (50 g) were left overnight for complete dissolution; the solution was then stirred and heated to 70°C under a nitrogen atmosphere. When the desired

temperature was reached, GMA monomer (a known amount containing 1.5×10^{-4} mol BPO/g DHPVC) was added with continuous stirring at 70°C. The reaction was carried out for predetermined periods. The mixture was then cooled and poured into an excess of well-stirred methanol. The precipitated polymer was filtered and washed several times with methanol and then dried to a constant mass at 50°C under a vacuum. The precipitate was a mixture of grafted copolymer PVC-g-GMA and poly(GMA). Poly(GMA) was removed by a Soxhlet extractor with acetone as the solvent. The remaining solid PVC-g-GMA was dried under a vacuum and weighed. The grafting parameters were estimated from the mass of the sample before and after grafting.

The fraction of grafting was calculated according to the relation

% grafting

$$= \frac{\text{mass of grafted polymer}}{\text{mass of grafted copolymer}} \times 100\% \quad (1)$$

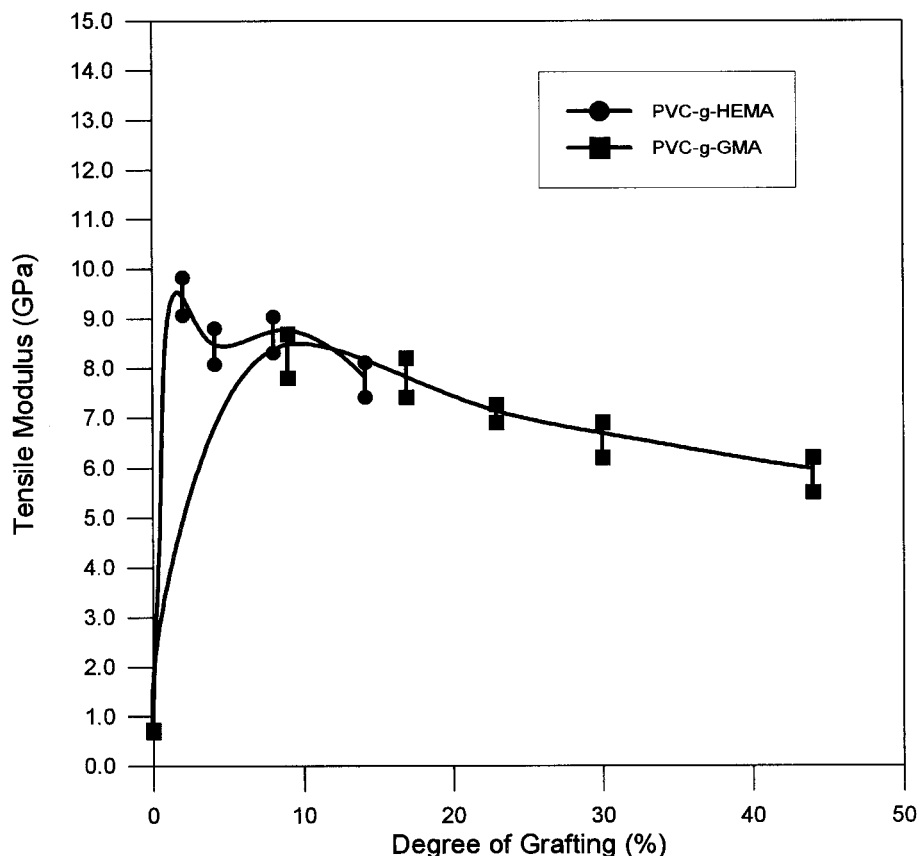


Figure 4 The change in tensile modulus for PVC-*g*-GMA and PVC-*g*-HEMA graft copolymers with various degrees of grafting.

PVC-*g*-HEMA Grafted Copolymerization and Separation

A typical graft copolymerization of DHPVC with HEMA is shown as follows.²³ First DHPVC (5 g) and solvent (50 g) were left overnight for complete dissolution; the solution was then stirred and heated to 70°C under a nitrogen atmosphere. When the desired temperature was reached, HEMA monomer (a known amount containing 1.5×10^{-4} mol BPO/g DHPVC) was added with continuous stirring at 70°C. The reaction was carried out for predetermined periods. The mixture was then cooled and poured into an excess of well-stirred *n*-hexane. The precipitated polymer was filtered and washed several times with *n*-hexane and then dried to a constant mass at 50°C under a vacuum. The precipitate was a mixture of grafted copolymer PVC-*g*-HEMA and poly(HEMA). Poly(HEMA) was removed by Soxhlet extraction with methanol as the solvent. The remaining solid PVC-*g*-HEMA was dried under a vacuum in an oven. The residue was precipitated with distilled

water. The recovered poly(HEMA) was dried and weighed. The grafting parameters were estimated from the mass of the sample before and after grafting. The fraction of grafting was calculated according to eq. (1).

Synthesis of Blocked Diisocyanates

A four-necked flask equipped with an electric stirrer, a reflux condenser, a dropping funnel, and an inlet gas blanket was charged with IPDI [56.49 g (0.3 mol)] and 10 mL DMAc.²⁴ The temperature was kept at 10°C using an ice bath. MEKO [26.136 g (0.3 mol)] was then added dropwise into the flask from a dropping funnel with stirring under a nitrogen atmosphere. The temperature was raised to 40°C after the adding of MEKO, and 0.90 g (1 wt %) of dibutyltin diacetate was added as a catalyst. The mixture was stirred and kept at 40°C for 1 h before the temperature was raised to 60°C. The solution of TMP [13.404 g (0.1 mol)] dissolved in 20 mL DMAc was dropped slowly into

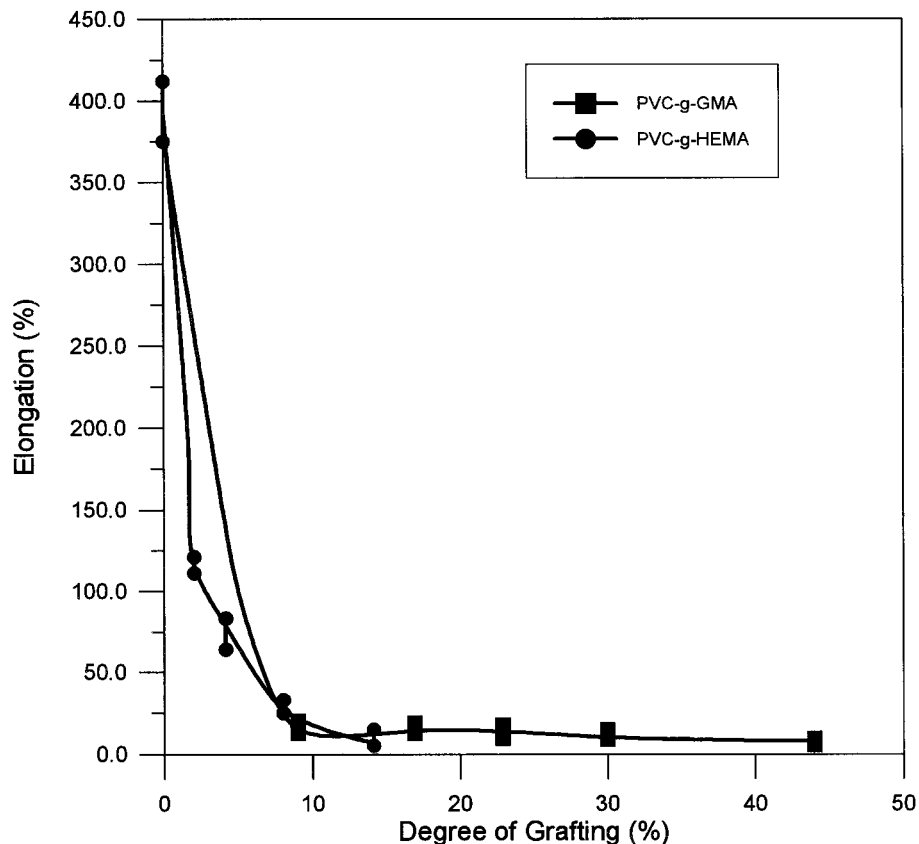


Figure 5 The change in elongation for PVC-*g*-GMA and PVC-*g*-HEMA graft copolymers with various degrees of grafting.

the flask. Then the temperature was raised to 90°C for 5 h. Some DMAc was added into the flask after the reaction was complete. The product, a golden viscous liquid at room temperature, is referred to here as a MEKO blocked IPDI [TMP(IPDI-MEKO)₃] (solid content 30.5%). The blocking and deblocking reactions for MEKO-blocked DI are shown in Scheme 1.

Preparation of Polymer Films

About 1 g of various polymers [PVC-poly(GMA), PVC-poly(HEMA), PVC-*g*-GMA, and PVC-*g*-HEMA] was dissolved in 10 mL of DMAc. The solution was poured into a 9-cm diameter Petri dish, which was placed in a 70°C oven for 24 h to remove the solvent. Then the obtained semidried polymer film was further dried at 100°C for 8 h under a vacuum.

Curing Reaction of Polymer Blend and Grafted Copolymer

Curing Reaction of PVC-Poly(GMA) Blends

The PVC-poly(GMA) blend (1.0 g) was dissolved in DMAc (10 mL); an equivalent diamine (4,4'-

diaminodiphenyl ether) curing agent, of which the quantity was taken according to the epoxide equivalent of PVC-poly(GMA), was weighed and added to the solution. After it dissolved, the solution was poured into a 9-cm diameter Petri dish and placed in an oven that had reached the reaction temperature.

Curing Reaction of PVC-*g*-HEMA and PVC-Poly(HEMA) Blend

A grafted copolymer (1.0 g) or PVC/poly(HEMA) blend was dissolved in DMAc (15 mL); an equivalent weight of curing agent (MEKO blocked DIs), of which the quantity was taken according to the OH equivalent of PVC-*g*-HEMA, was weighed and added to the solution. After it dissolved, the solution was poured into a 9-cm diameter Petri dish and kept at 100°C in an oven for 20 min to remove excess solvent. The temperature of the oven was raised to the deblocking temperature (150°C) for 25 min to cure it.

Measurements of Mechanical Properties

An Instron Universal tester model 1130 with a load cell of 5 kg was used to study the stress-

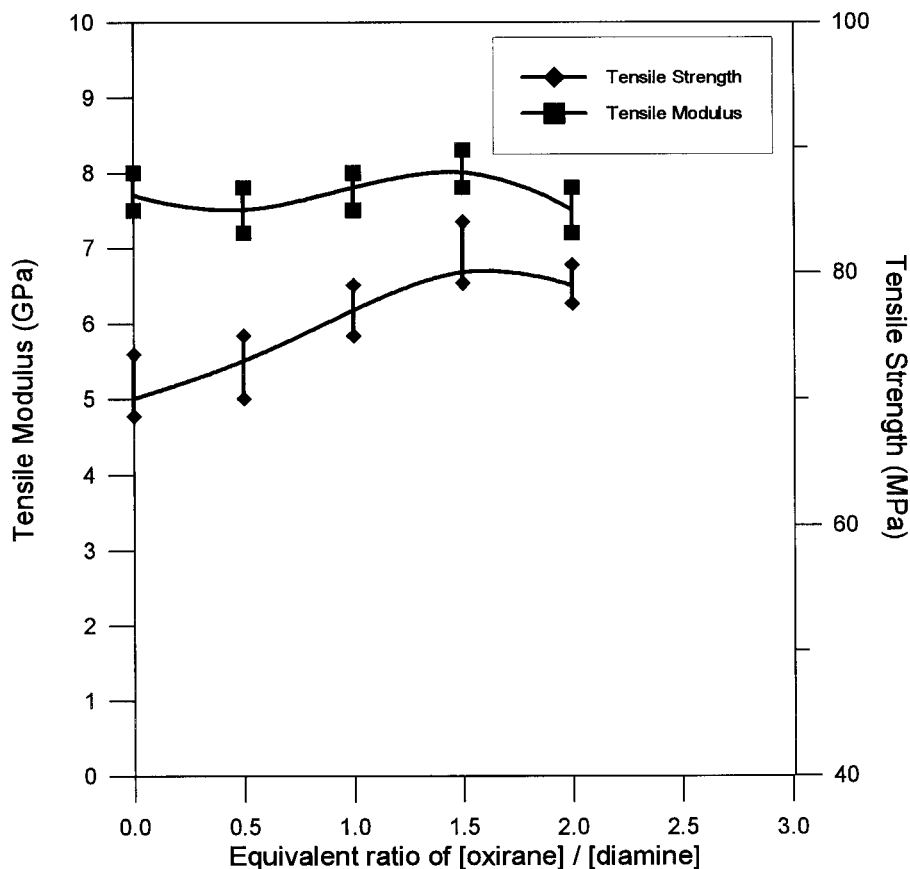


Figure 6 The change in tensile strength and modulus for PVC-poly(GMA) blend (PVC = 90%) crosslinked with various equivalent ratios of [oxirane]/[diamine].

strain behavior of the samples. A gauge length of 2 cm and strain rate of 5 cm/min were used in this study. The measurements were performed at room temperature using solution casting to obtain a film specimen. The dimensions of the specimen were 0.5-cm width, 6-cm length, and 0.1-mm thickness.

RESULTS AND DISCUSSION

The range of compatibility of PVC-poly(GMA) and PVC-poly(HEMA) blend systems reported in a previous study were successfully predicted by using the additivity of the slope for the plot of reduced viscosity versus the polymer concentration in the blend system. The range of compatibility for the PVC and poly(GMA) blend system had a PVC content larger than 76 wt % in the blend, and the range of compatibility for the PVC and poly(HEMA) had a PVC content greater than 90 wt %.³ Investigation of the mechanical properties

of the blends and graft copolymers for the said two polymers in the compatible range is described in this section.

Mechanical Properties of Grafted Copolymers and Polymer Blends

For the grafted copolymers and their polymer blends, Figures 1 and 2 show, respectively, the comparison of the tensile strength between PVC-*g*-GMA and PVC-poly(GMA), and between PVC-*g*-HEMA and PVC-poly(HEMA) at various weight percentages of GMA and HEMA. The result shown in Figure 1 indicates that the tensile strength for PVC-poly(GMA) blends is higher than that for the PVC-*g*-GMA graft copolymers. However, this is contrary to PVC-poly(HEMA) blends and PVC-*g*-HEMA graft copolymers (shown in Fig. 2). This contrary result may be due to the influence of the compatibility of polymer-polymer pairs such as PVC and poly(GMA) or PVC and poly(HEMA). For polymer blends the

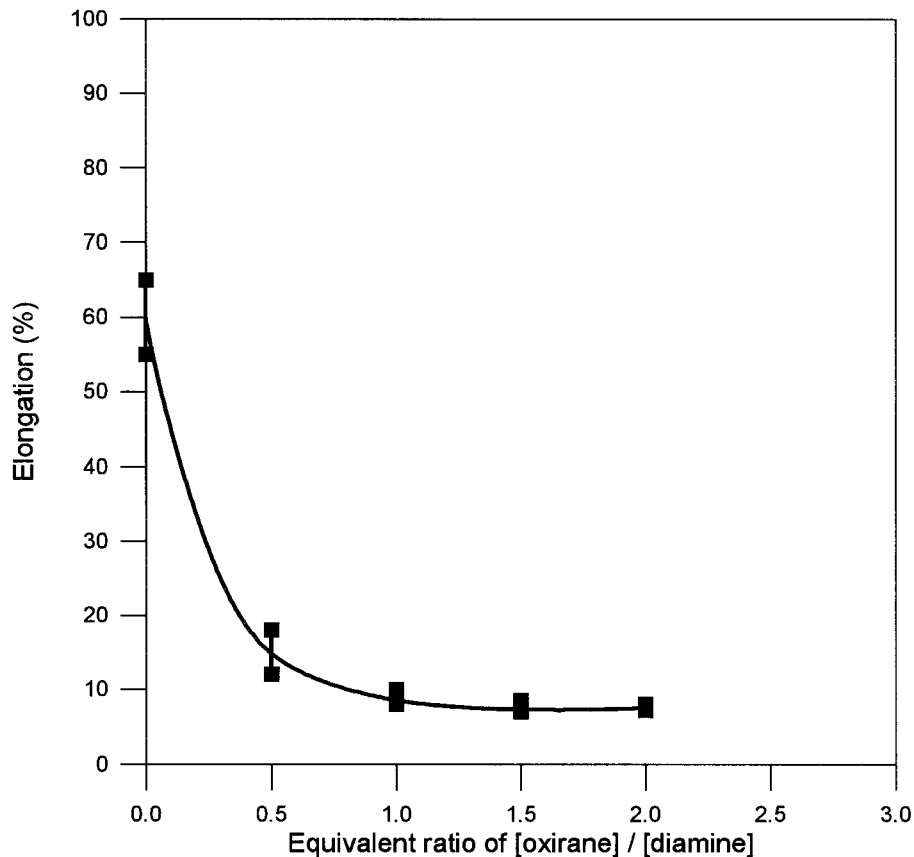


Figure 7 The change in elongation for PVC-poly(GMA) blend (PVC = 90%) cross-linked with various equivalent ratios of [oxirane]/[diamine].

mechanical properties are profoundly affected by the properties of the constituents of the blends and the degree of compatibility of the polymer blends, but usually the latter is a major factor in determining the final properties of a blend. Most polymer-polymer pairs are incompatible or have narrow compatible ranges in their blends, so the polymer blends are usually replaced with a grafted copolymer to improve physical properties. For a more compatible system, such as PVC and poly(GMA), the tensile strength is stronger for blends than for grafted copolymer (PVC-*g*-GMA) (see Fig. 1), but the tensile strength is weaker for blends than for grafted copolymer for a less compatible system [PVC-poly(HEMA) pairs]. From the above results we can conclude that if the compatible range is narrower for a polymer pair, the tensile strength of a graft copolymer is higher.

Mechanical Properties of Grafted Copolymers

The effect of the percentage of grafting for PVC-*g*-GMA and PVC-*g*-HEMA on tensile strength,

tensile modulus, and elongation are shown in Figures 3, 4, and 5, respectively. It is evident that the tensile strength increases with the degree of grafting to a maximum value at a degree of grafting of around 4% for PVC-*g*-HEMA and 10% for PVC-*g*-GMA. Thereafter, the tensile strength tends to decrease at higher degrees of grafting. Similarly, the tensile modulus increases with the degree of grafting to a maximum value at a degree of grafting of around 2% for PVC-*g*-HEMA and 10% for PVC-*g*-GMA. Thereafter, the modulus tends to decrease at higher degrees of grafting. The elongation decreases with an increase in the degree of grafting. The grafting of GMA or HEMA onto PVC films results in an appreciable improvement in the tensile strength, but the elongation generally decreases as the percentage of grafting increases.

The increase of the tensile strength and tensile modulus and the decrease of the elongation for a grafted copolymer may be attributed to the grafting of side chains onto the PVC main chain. The PVC main chain is entangled by the long chain

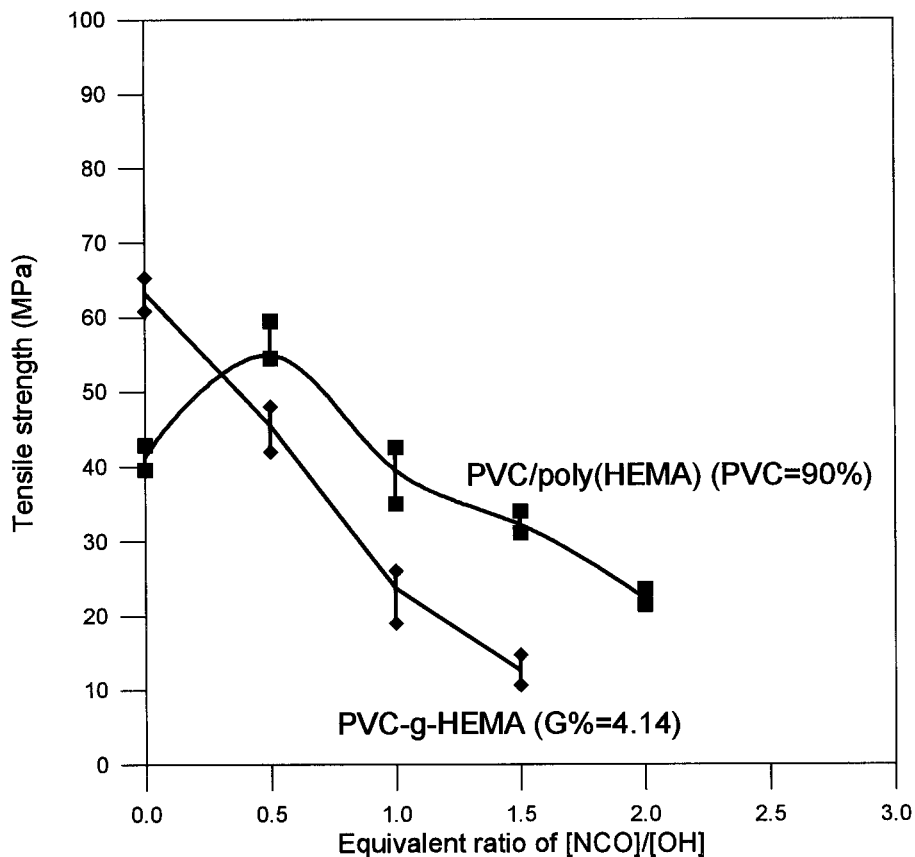


Figure 8 The change in tensile strength for PVC-*g*-HEMA copolymer (grafting = 4.14%) and PVC-poly(HEMA) polymer blend (PVC = 90%) crosslinked with various equivalent ratios of [NCO]/[OH].

graft that acts like a crosslinked network structure in PVC. The rigidity of PVC increases with increasing content of grafted chains; therefore, the tensile strength and tensile modulus increase but elongation decreases.

In addition, from the viewpoint of the glass transition temperature (T_g), the T_g values are increased with an increase of the HEMA content on the PVC-*g*-HEMA grafts and the T_g values are decreased with an increase of the GMA content on the PVC-*g*-GMA grafts according to our previous reports.^{22,23} Hence, the tensile strength and modulus for the higher T_g graft (PVC-*g*-HEMA) are greater than those for lower T_g grafts (PVC-*g*-GMA), and the elongation for both graft copolymers shows a sharp decrease at higher grafting degrees.

Mechanical Properties of PVC-Poly(GMA) Cured with Curing Agent

The changes in tensile strength, tensile modulus, and elongation at break for the PVC-poly(GMA)

polymer blends (PVC = 90%) cured with diamine were investigated and the results are shown in Figures 6 and 7, respectively. The tensile strength and modulus for polymer blends (PVC = 90%) cured with diamine at various ratios of the [amino group]/[oxirane group] are slightly higher than those of pure polymer blends. The elongation decreases with an increase of the ratio of the [amino group]/[oxirane group]. The curing behavior of PVC-poly(GMA) with diamine results in appreciable improvement in the tensile strength and modulus, but the elongation generally decreases as the ratio of [amino group]/[oxirane group] increases.

The slightly improvement in tensile strength and tensile modulus is caused by the limited crosslinked network structure that can be reasonably explained by the narrow compatible range for PVC and poly(GMA) and the low curing efficiency of the oxirane group and amino group.²³ In addition, the rigidity of the PVC-poly(GMA) polymer blend also increased with the formation

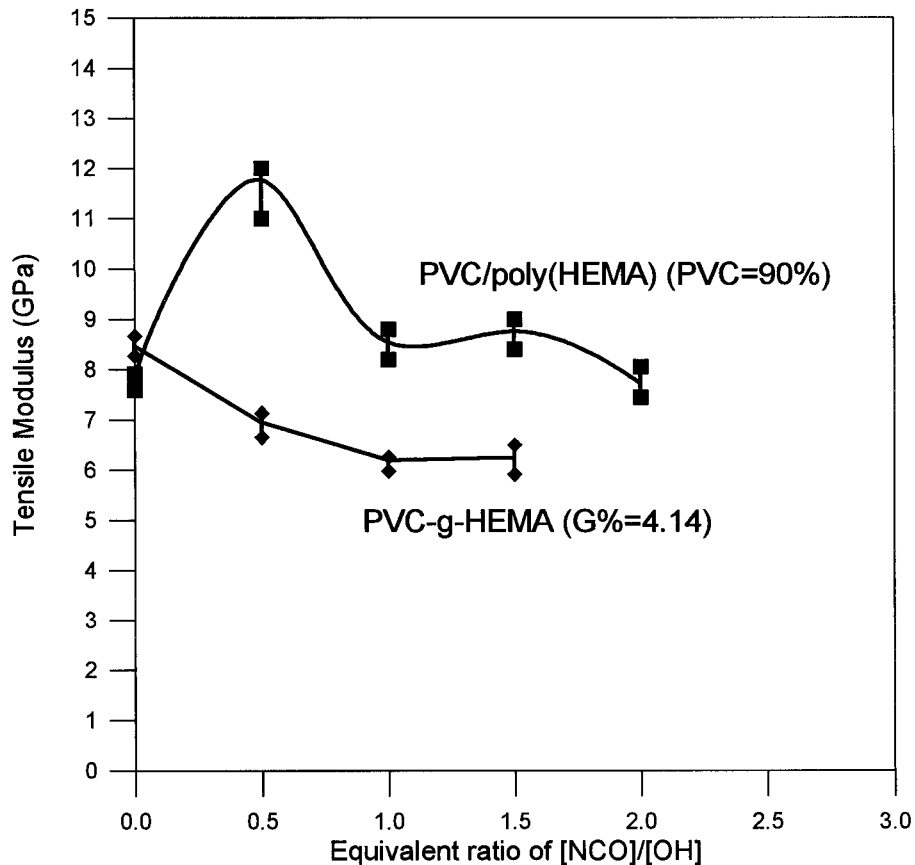


Figure 9 The change in tensile modulus for PVC-g-HEMA copolymer (grafting = 4.14%) and PVC-poly(HEMA) polymer blend (PVC = 90%) crosslinked with various equivalent ratios of [NCO]/[OH].

of a crosslinked network structure; therefore, the tensile strength and tensile modulus increase and the elongation decreases.

Mechanical Properties of PVC-g-HEMA or PVC-Poly(HEMA) Cured with Curing Agent

The changes in tensile strength, tensile modulus, and elongation at break were investigated for the PVC-g-HEMA copolymer (grafting = 4.14%) and for the PVC-poly(HEMA) polymer blends (PVC = 90%) cured with [TMP(IPDI-MEKO)₃] as the crosslinking agent. The results are shown in Figures 8, 9, and 10, respectively. Because the films of PVC-g-HEMA cured with various concentrations of crosslinking agent are embrittled, the tensile strength, tensile modulus, and elongation decrease with the increasing ratio of [NCO]/[OH]. But for PVC-poly(HEMA) blends it is found that the tensile strength and modulus increase with an increasing ratio of [NCO]/[OH] to a maximum

value at a ratio of [NCO]/[OH] of around 0.5. Thereafter the tensile strength and tensile modulus tend to decrease at a higher ratio of [NCO]/[OH]. The elongation decreases with an increase of the ratio of [NCO]/[OH]. Because low curing efficiency (50% gel content approached) for PVC-g-HEMA cured with MEKO blocked DI was reported in a previous article,²⁴ the degree of grafting for HEMA grafted onto PVC is low for the present system and the degree of crosslinking for said graft is much lower. On the other hand, the residue of the crosslinker will remain in the cured film when an excess of crosslinker is used. This occurrence will lead to the mechanical properties of the cured film being weaker and embrittled. But for the PVC and poly(HEMA) blend (PVC = 90%), because of the higher content of poly(HEMA) in the blend, the mechanical properties will be strengthened when the poly(HEMA) is crosslinked with crosslinker below the equivalent ratio of [NCO]/[OH] of 0.5. Similarly, the me-

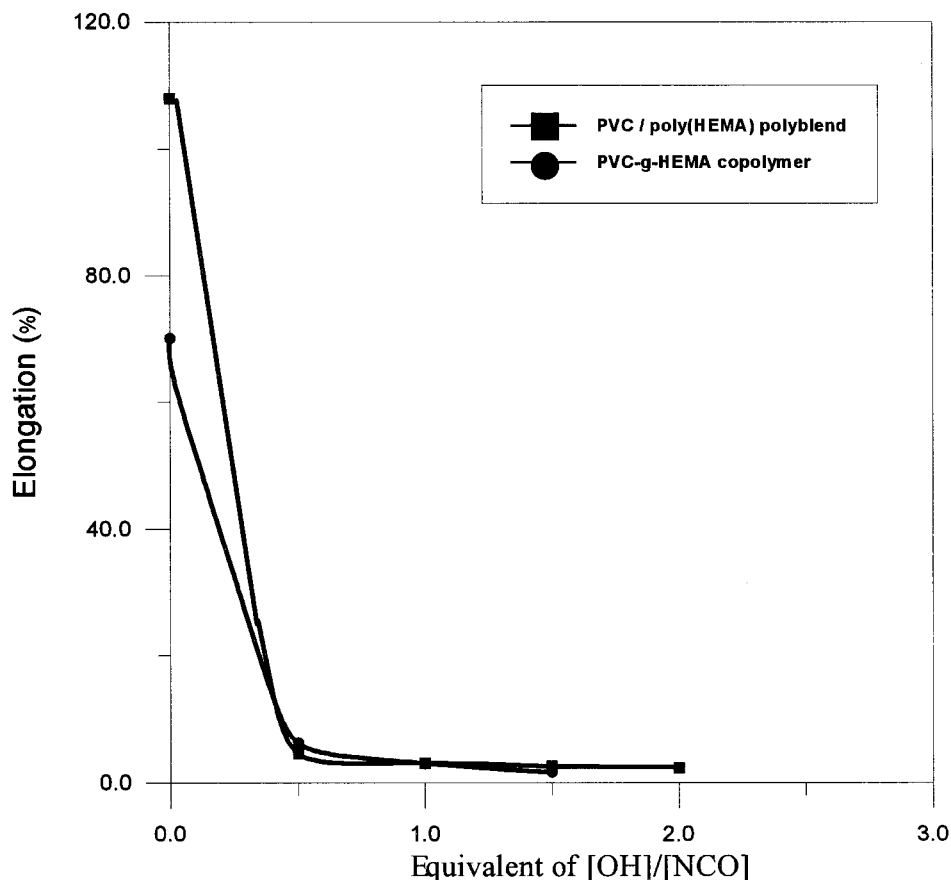


Figure 10 The change in elongation for PVC-*g*-HEMA copolymer (grafting = 4.14%) and PVC-poly(HEMA) polymer blend (PVC = 90%) crosslinked with various equivalent ratios of [NCO]/[OH].

chanical properties will be decreased when the equivalent ratio of [NCO]/[OH] is beyond 0.5.

Hydrophilicity of Grafted Copolymers and Polymer Blends

Because of hydrophilic groups ($-\text{OH}$) existing in HEMA, the hydrophilic ability of PVC will be improved in the grafted copolymer and polymer blend for PVC with HEMA. The improvement of the hydrophilic ability for PVC can be indicated by contact angle measurement between the polymer films and water drops. When the hydrophilic ability of the polymer films is increased, the interface tension between the films and water drops will be increased; then the water will easily permeate into the films and the contact angle between the films and water drops will decrease. The results of the contact angle measurements for various

PVC-poly(HEMA) polymer blends and PVC-*g*-HEMA grafted copolymers are shown in Figure 11. The contact angles of PVC-*g*-HEMA grafted copolymers are all smaller than those for PVC-poly(HEMA) polymer blends. These results show the improvement of hydrophilicity for the grafted copolymer containing the hydrophilic side chain. It is better than that for the polymer blends for which hydrophilic polymer is dispersed into the hydrophobic polymer.

CONCLUSION

The mechanical properties for polymer blends are obviously affected by the compatibility of the polymer pairs. In the more compatible system (PVC and GMA), the PVC-poly(GMA) blends have better mechanical properties than the corresponding graft copolymers. The mechanical properties

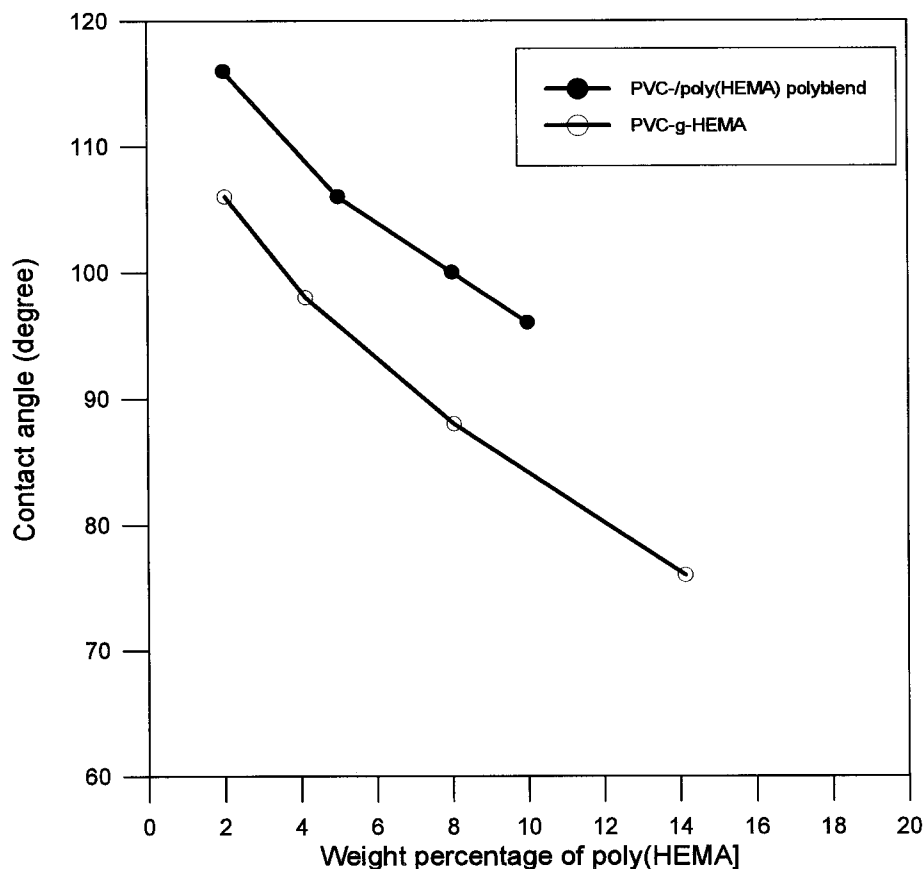


Figure 11 The comparison of contact angle between PVC-poly(HEMA) blends and PVC-g-HEMA grafts containing various weights of HEMA.

for PVC-poly(HEMA) blends are worse than those for the PVC-g-HEMA graft copolymers in the lower compatibility system. The mechanical properties for PVC-poly(GMA) blend systems are not affected by crosslinking of the blend systems, but those for PVC-poly(HEMA) and their graft copolymers are decreased with an increase of the equivalent ratio of $([NCO]/[OH])$ of the crosslinker. The contact angle test shows that the hydrophilicity for grafted copolymer is better than for polymer blends.

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