

Investigation of the Compatibility for PVC Blend by Reduced Viscometric Method

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ABSTRACT: A new method is presented to predict the compatibility of a polymer blend. The compatibility of the polymer–polymer pairs containing poly(vinyl chloride) (PVC), poly(glycidyl methacrylate) [poly(GMA)], poly(methyl methacrylate) [poly(MMA)], and poly(styrene) (PS) predicted by the use of the deviation from the additivity law of the slope in the reduced viscosity (η_{sp}/C) versus polymer concentration (C) plot of a binary blend system is the purpose of this article. In addition, the influence of the grafted copolymer (PVC-*g*-GMA) on the compatibility of PVC–poly(GMA) pairs is also investigated by this reduced viscosity method and also confirmed by the differential scanning calorimetric technique. The results contrasted to the thermodynamic principle showed that the polymer blends could be considered to be a compatible blend when the deviation values deviated from the additivity law of the slopes in the η_{sp}/C vs. C plot are smaller than 15%. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 761–775, 1997

Key words: PVC blend; compatibility; reduced viscometric method

INTRODUCTION

Polymer blends are physical mixtures of structurally different polymers that interact through secondary forces but not covalent bonding.^{1,2} The importance of blending has increased recently because its superiority over homopolymers can be analogical to those of alloys over metals. While many of polymer blends cannot be called alloys, they must be considered as polymer mixtures having various degrees of compatibility. The degree of compatibility usually determines the final properties of the blend.^{2,3}

The compatibility of polymer blends has been examined by sophisticated experimental and theoretical techniques. The determination of heat of mixing, glass transition temperatures (T_g), and morphology by scanning electron microscopy (SEM) and dynamic mechanical response are

some methods extensively reported in the literature.^{4–6} Besides, the degree of compatibility in polymer blends is dependent on the polymer–polymer molecular interaction, and the viscosity is also reflected by the degree of compatibility. While in solution, the macromolecules of a blend may exist in a molecularly dispersed state and undergo mutual attraction or repulsion, thereby rendering positive or negative influence on viscosity. Interactions among blending constituents are reflected in solution viscosity because polymer–polymer interactions usually dominate over polymer–solvent interaction. Some methods used to access the compatibility were reported for the studies of the viscosities of polymer mixtures in solution,^{1–3,7–18} such as Kuleznev et al.¹⁸ and Hourston and Hughes,⁸ who presented the viscometric and sonic velocity measurements, respectively. Singh and Singh² presented the measurement of ultrasonic viscosity for compatible and incompatible blends, and Feldman and Rusu⁷ presented the dynamic viscosity measurements.

For novel polymer blends, one cannot find the

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Table I The Characteristic Data of Polymers and Monomer Used for ΔH_m

Sample	Solubility Parameter (δ) ^a	Density (ρ)	Number-average Molecular Weight (M_n)
PVC	9.45	1.44	65,000
Poly(GMA)	10.22	1.25	143,000
Poly(MMA)	9.10	1.18	140,000
PS	8.6	1.12	100,000
THS	9.1	—	—
Vinyl chloride	—	—	62.5
GMA	—	—	142.15
MMA	—	—	100.12
Styrene	—	—	104.07

^a The data of δ was obtained from polymer handbook.

compatibility from their solubility parameters. However, the compatibility of polymer blends can be inferred by glass transition temperature or morphology, but these methods must be used by various very expensive instruments; and the viscosity methods presented in previous studies also need special viscosimeters, which do not corresponded to a quick and simple method for us.⁷⁻¹⁷

Recently, reduced viscosity is also referred to determine the degree of compatibility for polymer blends;³ the plot of reduced viscosity vs. concentration deviates from parallelism according to the compatibility of polymer blends, and the slopes for compatible system are parallel. Although these investigations offer a entirely quick and simple method for the compatibility of polymer blend, re-

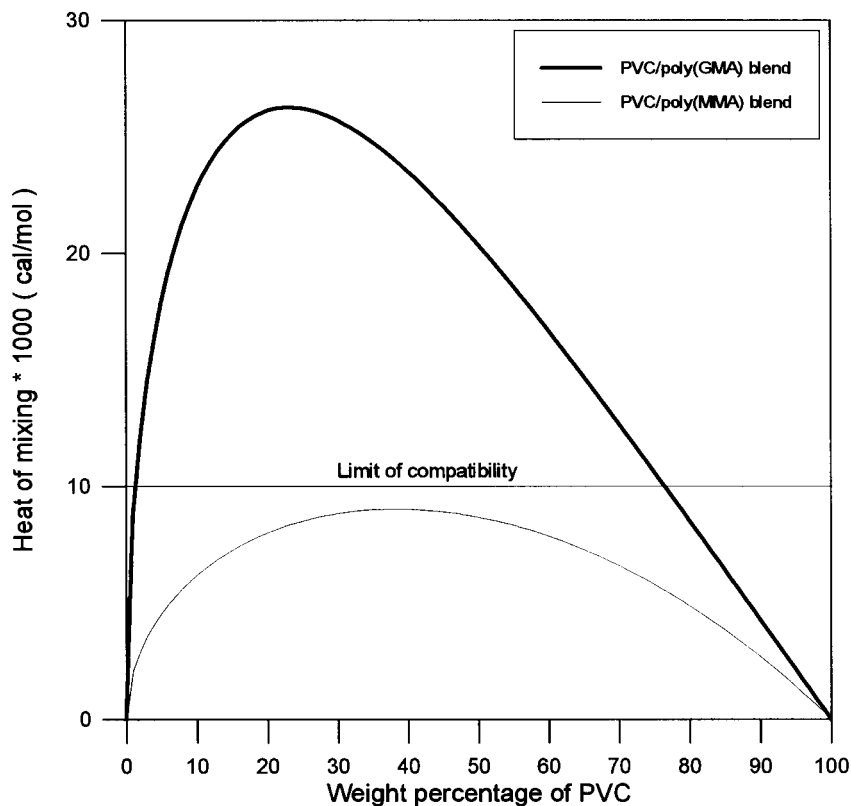


Figure 1 Heat of mixing vs. percentage of PVC in PVC-poly(MMA) and PVC-poly(GMA) polymer blends.

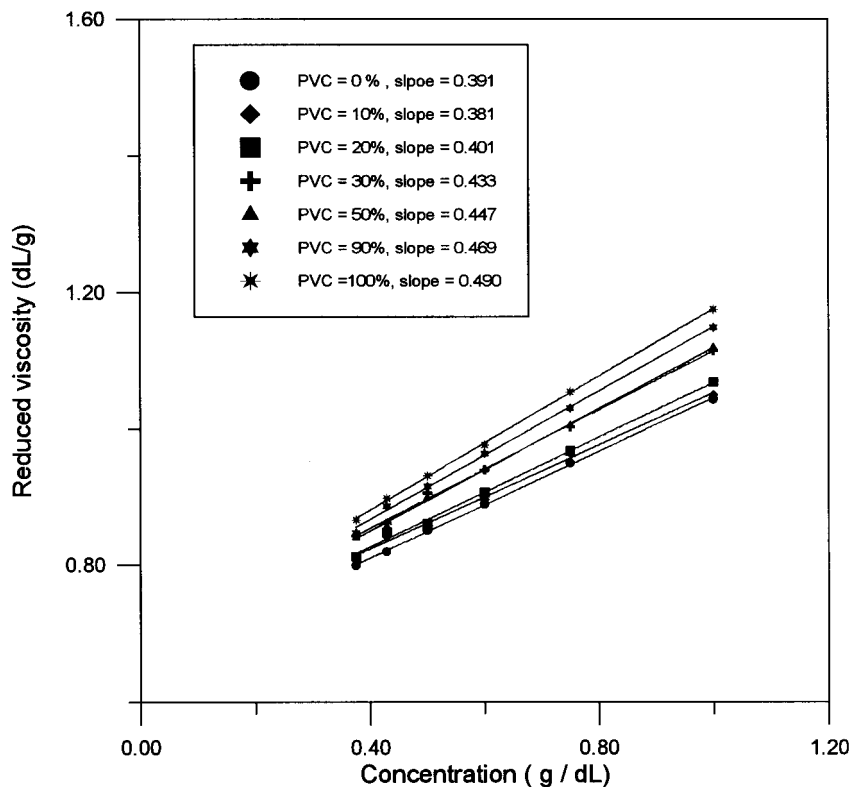


Figure 2 The plot of the reduced viscosity vs. concentration for PVC–poly(MMA) polymer blends.

relationships like this are not found in many blend systems so we attempt to offer a better, more reasonable method to determine the degree of compatibility in polymer blends. The Mark–Huggins equation is used to determine the degree of compatibility for the polymer blends through a new idea, and the slope of the plot in reduced viscosity vs. concentration may be reflected by polymer–polymer molecular interaction. Some known compatible and incompatible polymer blend systems containing poly(vinyl chloride) (PVC), poly(methyl methacrylate) [poly(MMA)], poly(glycidyl methacrylate) [poly(GMA)], and poly(styrene) (PS) are chosen to measure the slope of reduced viscosity vs. concentration in various compositions and to access the additivity of the slopes in various composition of each blend system. Finally, the compatibilization and T_g tests are presented to confirm the improvement of the compatibility in incompatible blends.

EXPERIMENTAL

Materials

PVC resin (S-70, DP = 1070) was supplied by Formosa Plastic Co. (Taiwan). Methyl methacry-

late (MMA), glycidyl methacrylate (GMA), and styrene monomers are distilled under reduced pressure. Benzoyl peroxide (BPO) was recrystallized by dissolving in chloroform at room temperature and precipitated by adding methanol. 1,4-Dioxane, acetone, cyclohexanone, and methanol were used as received.

Synthesis of Homopolymers

Preparation of Poly(GMA) Homopolymer

GMA (20 g), BPO (0.1 wt %), and 1,4-dioxane (50 mL) was introduced into a 100 mL round bottom vessel equipped with a stirrer, cooler, and thermometer under a nitrogen atmosphere. The polymerization was performed at 70°C for 6 h under stirring. After polymerization, the mixture was precipitated in methanol for 24 h. The product was then dried at 70°C for 24 h under vacuum oven. The product, poly(GMA), then dissolved and precipitated three times repeatedly for purification. The number-average molecular weight (\bar{M}_n) for poly(GMA) is 143,000 measured by gel permeation chromatography (GPC) (Waters model 410).

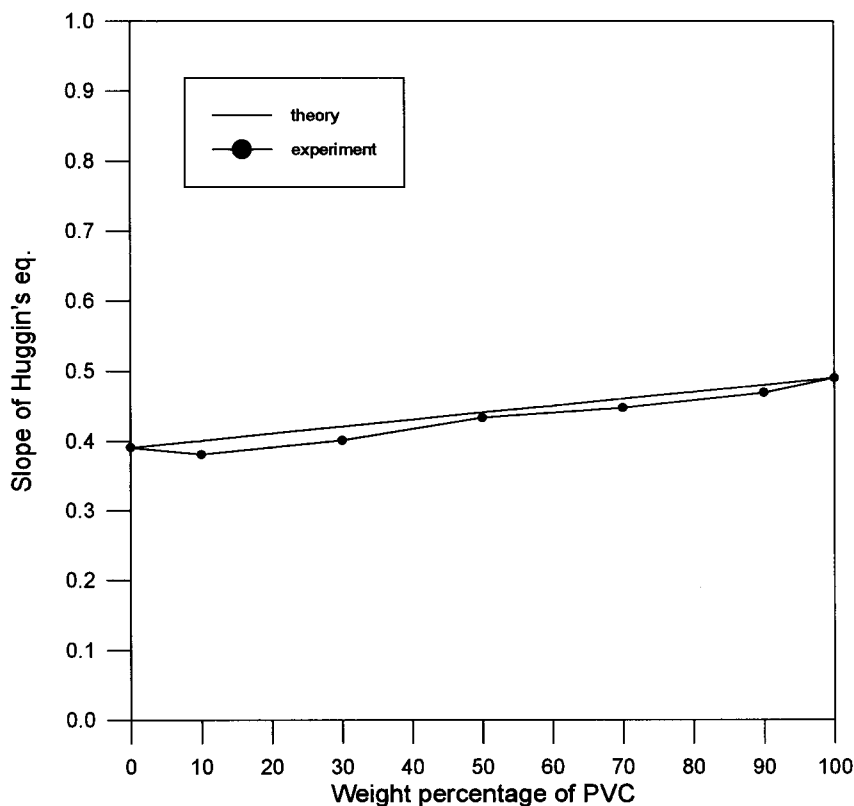


Figure 3 The plot of the reduced viscosity vs. concentration for PVC-poly(GMA) polymer blends.

Preparation of Poly(MMA) Homopolymer

MMA (20 g), BPO (0.1 wt %), and THF (50 mL) was introduced into a 100 mL round bottom vessel equipped with a stirrer, cooler, and thermometer under a nitrogen atmosphere. The polymerization was carried out at 75°C for 7.5 h under stirring. After polymerization, the mixture was precipitated in methanol for 24 h. The product was then dried at 70°C for 24 h under vacuum in an oven. The product, poly(MMA), then dissolved and precipitated three times repeatedly for purification. The number-average molecular weight (\bar{M}_n) for poly(MMA) is 140,000 measured by GPC (Waters model 410).

Preparation of Poly(styrene) Homopolymer

Styrene (20 g), BPO (0.1 wt %), and benzene (30 mL) was introduced into a 100 mL round bottom vessel equipped with a stirrer, cooler, and thermometer under a nitrogen atmosphere. The polymerization was conducted at 75°C for 7.5 h under stirring. After polymerization, the mixture was precipitated in methanol for 24 h. The product

was then dried at 70°C for 24 h under vacuum in an oven. The product, poly(styrene), was then dissolved and precipitated three times repeatedly for purification. The number-average molecular weight (\bar{M}_n) for poly(styrene) is 100,000 measured by GPC (Waters model 410).

Synthesis of PVC-g-GMA Grafted Copolymer

Preparation of Dehydrochlorinated PVC (DHPVC)

A weighed quantity of PVC resin and 10 times its amount of 10% NaOH solution in mass were fed into a round bottom flask fitted with a reflux condenser. 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 dehydrochlorinated PVC (DHPVC).

Grafted Polymerization and Separation

The graft polymerization and separation of PVC-g-GMA graft copolymer was described in elsewhere.¹⁹

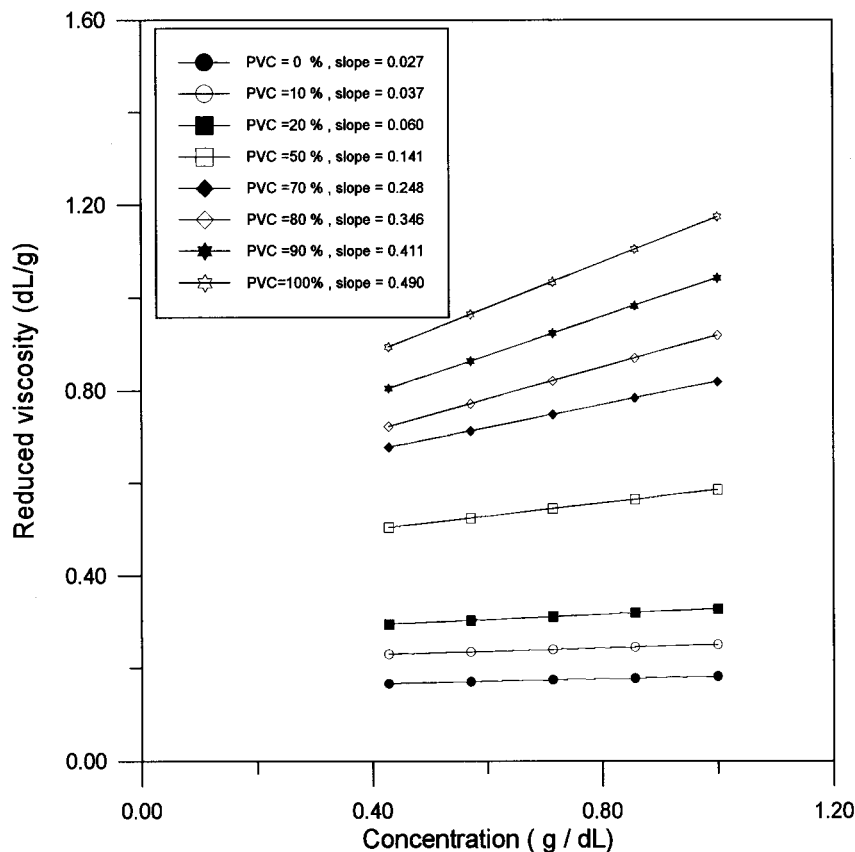


Figure 4 The comparison of additivity of slope between theory and experiment based from Huggin's equation in PVC-poly(MMA) polymer blends.

Viscometric Measurements

Viscometric measurements were carried out with an Ubbelodhe viscometer (flow time was 77.71 s for pure water) at $30 \pm 0.01^\circ\text{C}$. The polyblend samples were dissolved in THF solution of varied compositions to yield stock solutions of approximately 1.0 g polymer per 100 mL solvent.

Viscosity data were calculated according to Mark-Huggins equation as follows:

$$\eta_{sp}/C = [\eta] + k'[\eta]^2C \quad (1)$$

where η_{sp} is the specific viscosity, C is the concentration of polymer blend, $[\eta]$ is the intrinsic viscosity, and k' is the Huggins constant. η_{sp}/C is plotted versus C ; and $[\eta]$ and k' are, respectively, determined from the intercept and the slope of the straight line.

DSC Measurements

Glass transition temperature (T_g) was determined by using a Dupont 2000 differential scan-

ning calorimeter. The sample was 8 mg of dried film. All samples were heated up to 150°C at heating rates of $10^\circ\text{C}/\text{min}$ and kept for 90 s at that temperature to remove the traces of solvent, then quenched to -50°C , and kept at that temperature for 5 min (as first scan), then reheated to 150°C from -50°C at a heating rate of $10^\circ\text{C}/\text{min}$ (as second scan). The T_g values adopted in this article were second scanning values.

RESULTS AND DISCUSSION

Thermodynamic Theory

According to thermodynamic principles, any solution process is governed by the free energy relationship, as follows:

$$\Delta G = \Delta H - T\Delta S \quad (2)$$

If a polymer dissolves spontaneously, the free energy of solution, ΔG , is negative. The entropy of

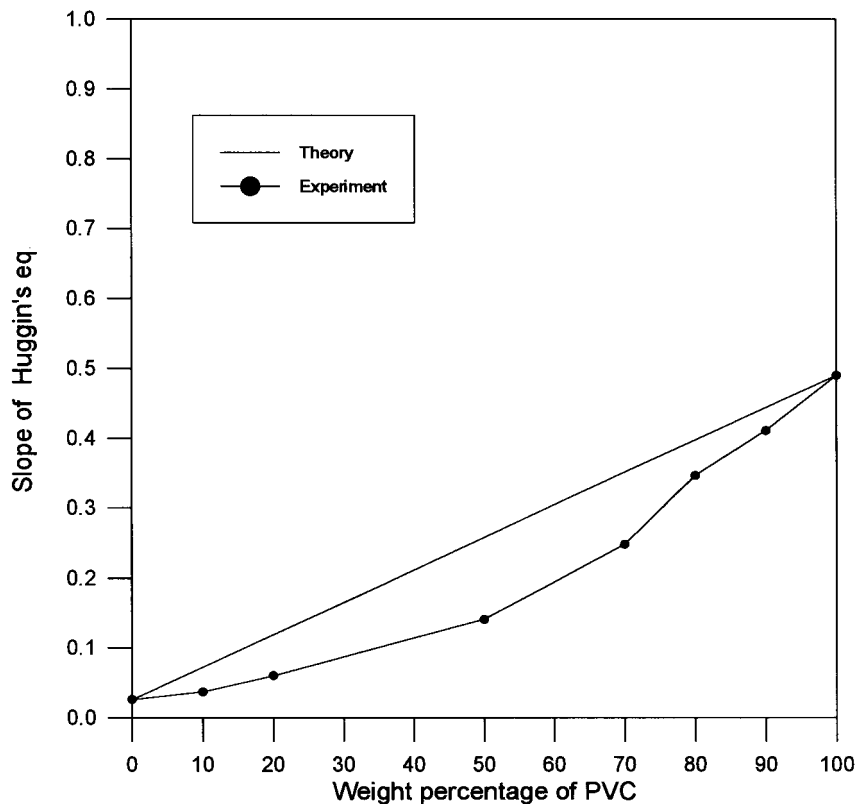


Figure 5 The comparison of additivity of slope between theory and experiment, based on Huggin's equation, in PVC-poly(GMA) polymer blends.

solution, ΔS , invariably has a positive value arising from increased conformational mobility of the polymer chains. Hence, the magnitude of the enthalpy of solution, ΔH , determines the sign of ΔG . Clearly, for the polymer to dissolve (negative ΔG), ΔH must be small. The equation of heat of mixing (ΔH_m) for one polymer dissolved in an organic solvent suggested by Gee²⁰ could be expressed as follows:

$$\Delta H_m = \{V_0(\delta_0 - \delta_1)^2(1 - v_0)^2\}^{1/2} \quad (3)$$

where V and δ are the molar volume and solubility parameter of the solvent 0 and the polymer 1, and the term $(1 - v_0)$ represents the volume fraction of the polymer. The relation of polymer-solvent interaction presented by Gee²⁰ was extended by Schneier²¹ to the polymer-polymer pairs interactions. Equation (3) was rewritten by Schneier as follows:

$$\Delta H_m = \{V_1(\delta_1 - \delta_2)^2(1 - v_1)^2\}^{1/2} \quad (4)$$

where V_1 and v_1 are the molar volume and volume fraction of polymer 1, respectively; the term $(1 - v_1)$

represents the volume fraction of polymer 2 in the mixture; and δ_1 and δ_2 are the solubility parameters of polymers 1 and 2, respectively. Because there is a given weight, X , of polymer in every mixture, $(X_1/M_1)/\rho_1 = V_1$ represents the molar volume fraction of polymer 1, where M and ρ are the molecular weight of an average monomer unit and density, respectively. The volume fraction v_1 of polymer 1 presented in the system is given by

$$v_1 = \frac{(X_1/M_1)/\rho_1}{(X_1/M_1)/\rho_1 + (X_2/M_2)/\rho_2} \quad (5)$$

and

$$1 - v_1 = \frac{X_2 M_1 \rho_1}{X_1 M_2 \rho_2 + X_2 M_1 \rho_1} \quad (6)$$

where $X_1 + X_2 = 1$, substituting this value into eqs. (6) and (4), eq. (7) is obtained as follows:

$$\Delta H_m = \left\{ X_A M_A \rho_A (\delta_A - \delta_B)^2 \times \left[\frac{X_B}{(1 - X_B) M_B \rho_B + (1 - X_A) M_A \rho_A} \right]^2 \right\}^{1/2} \quad (7)$$

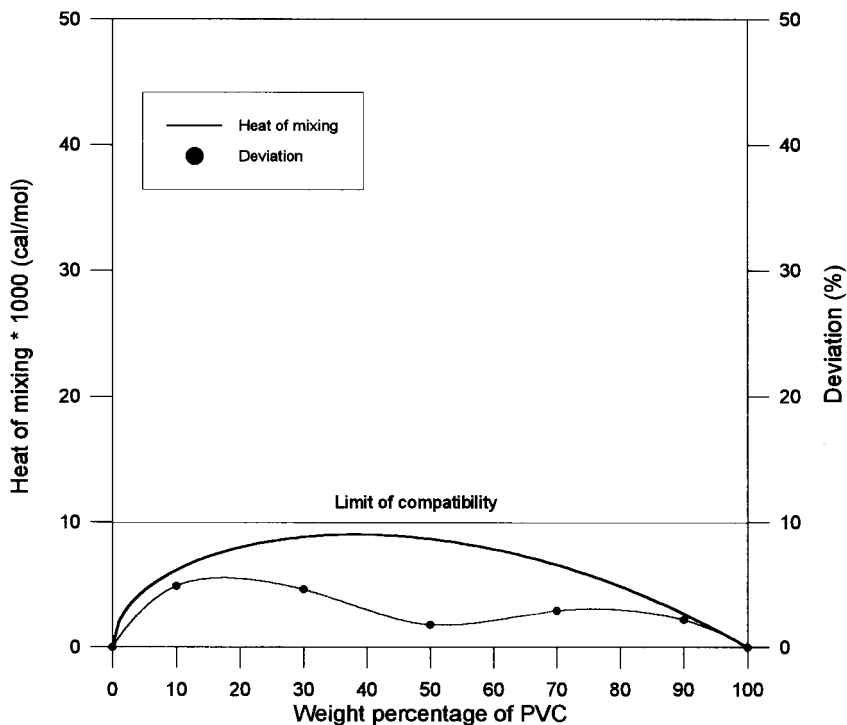


Figure 6 The comparison between the deviation of the additivity of reduced viscosity and heat of mixing in PVC–poly(MMA) polymer blends.

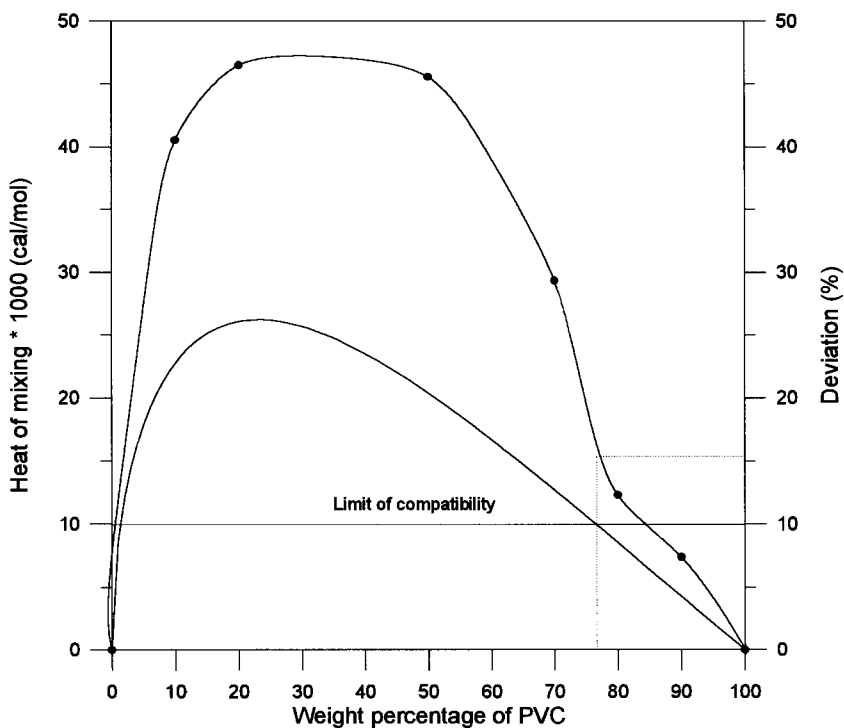


Figure 7 The comparison between the deviation of the additivity of reduced viscosity and heat of mixing in PVC–poly(GMA) polymer blends.

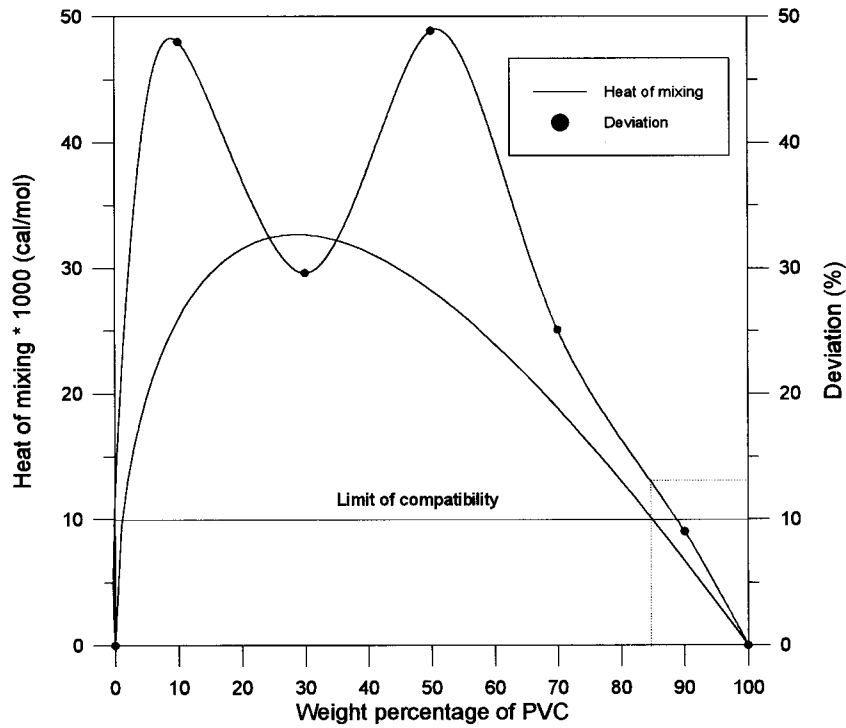


Figure 8 The comparison between the deviation of the additivity of reduced viscosity and heat of mixing in PVC/PS polymer blends.

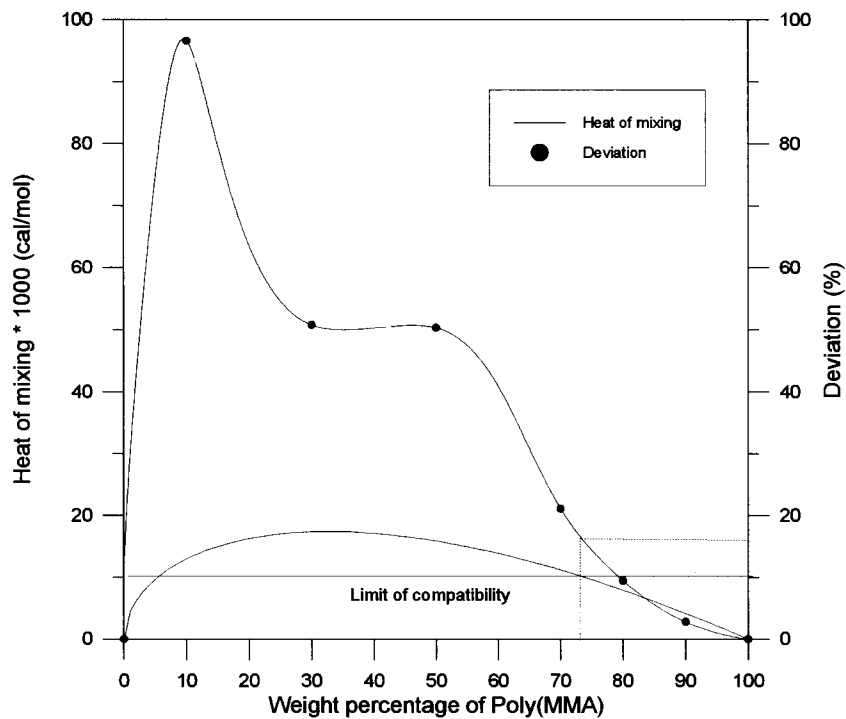


Figure 9 The comparison between the deviation of the additivity of reduced viscosity and heat of mixing in PS/poly(MMA) polymer blends.

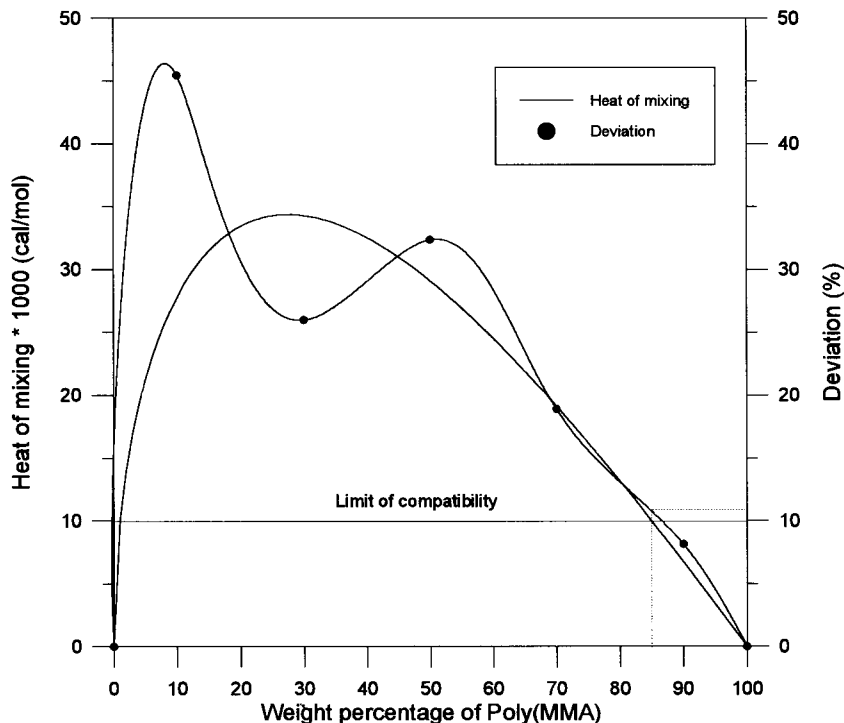


Figure 10 The comparison between the deviation of the additivity of reduced viscosity and heat of mixing in poly(GMA)/poly(MMA) polymer blends.

In order to use eq. (7), values are needed for the solubility parameter, density, and molecular weight of an average unit of the polymer. The validity of the eq. (7) was tested using the data of Bohn,⁵ who listed the polymer pairs under the heading of first and second components. When the polymer systems are compatible, the value of ΔH_m lies in the range of from 1×10^{-3} to 10×10^{-3} cal mol.^{3,5}

The data shown in Table I are substituted in eq. (7). The results are shown in Figure 1. The results obtained from Figure 1 indicate that the

heat of mixing for PVC–poly(MMA) blends, which are compatible in all compositions, are smaller than 10^{-2} cal mol, but the heat of mixing for PVC/poly(GMA) blends are incompatible when the composition of PVC is smaller than 76 wt %.

Viscosity Measurements

In order to confirm the results obtained from the thermodynamic principle mentioned above, the reduced viscosity measurement is adopted and at-

Table II Compatible Ranges for Some Polymer Pairs Accessed From Thermodynamic Method and Presented Reduced Viscosity Method

Component 1	Component 2	Compatible Range	
		Thermodynamic Method (ΔH_{mix})	Presented in This Article
PVC	Poly(MMA)	Completely miscible	Completely miscible
PVC	PS	> 84%	> 82%
PVC	Poly(GMA)	> 78%	> 76%
Poly(MMA)	PS	> 73%	> 75%
Poly(MMA)	Poly(GMA)	> 78%	> 76%

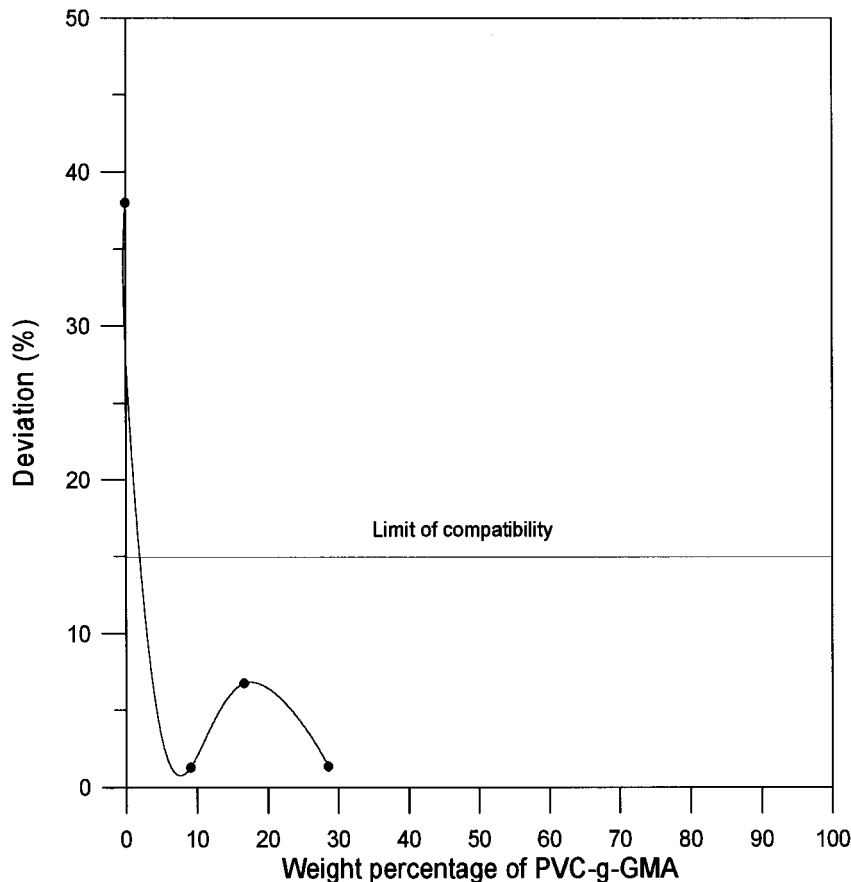


Figure 11 The improvement of PVC–poly(GMA) blend system (PVC = 60%) by PVC-g-GMA (grafting = 16.9%) compatibilization agent based on the reduced viscosity method.

tempted to elucidate the compatibility of the polymer blends. The reduced viscosity method was presented by Kulshreshtha et al.³ They reported that a linear parallel relationship was obtained for a compatible blend systems (ABS–PVC), i.e., the slope of respective blend composition in the plot of reduced viscosity versus polymer concentration has the same value. According to this viewpoint, completely compatible PVC–poly(MMA) blend systems and incompletely compatible PVC–poly(GMA) blend system are used to investigate. The result are shown in Figures 2 and 3 for the PVC–poly(MMA) and PVC–poly(GMA) blend systems, respectively. But no parallel relationship for the compatible PVC–poly(MMA) system was observed, and the slopes in the plot of reduced viscosity versus polymer concentration for every composition of compatible or incompatible blend systems [(PVC–poly(MMA) and PVC–poly(GMA) blend systems] are not equal. From these results, Kulshreshtha's method requires

some correction. In addition, the compatible range of polymer blends will also be investigated. Hence, the additivity of the slope for the blend systems of the two pure polymers is presented to predict the compatibility of the blend system between two homopolymers.

The Additivity Law of Slope in the Reduced Viscosity Versus Polymer Concentration

The viscometric method presented by Kulshreshtha et al.³ indicated that if the slope in the reduced viscosity vs. polymer concentration plot of a blend at various compositions are equal to that in η_{sp}/C vs. C plot of a homopolymer, then the blend is compatible. But, in fact, it is not suitable for the compatible blends, which are reported on in the literature, such as PVC and poly(MMA) blend system;¹⁹ i.e., the slopes in the η_{sp}/C vs. C plot of a compatible blend are not equal, even though they are called compatible blends. Based on this

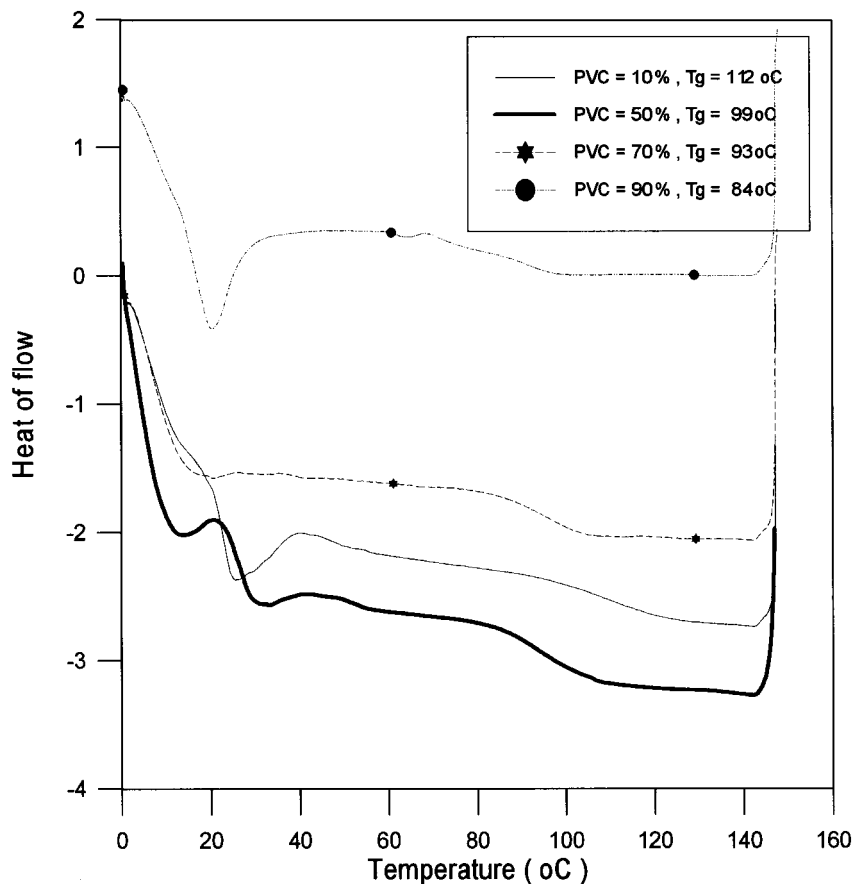


Figure 12 DSC curves for PVC-poly(MMA) polymer blends.

reason, the viscometric method would be modified in order to widely use for more polymer blend systems.

From the viewpoint of molecular level, the compatibility of a polymer blend is dependent on the molecular interaction between two polymers, these molecular interactions would be reflected in the viscosity in the dilute solution. Hence, if the blend is a compatible system, and the system has no molecular interaction in the solution, then the slope in the η_{sp}/C vs. C plot of the blend should have an additivity; and if the blend is an incompatible system, then the mutual attraction force or repulsion force between the polymers would make the sum of slopes in the η_{sp}/C vs. C plot of a blend be a positive or negative deviation from linear additivity. This behavior is analogical to the Raoult's Law,²² which states that the molecular interaction of mixed solution would influence the additivity of mixed vapor pressure of the solution.

Therefore, we present here the concept of the additivity law of the slope in a plot of the reduced

viscosity versus polymer concentration for the polymer blend and combine that the thermodynamic principle to judge the compatibility of the polymer blends. Figures 4 and 5 respectively show the relationship of the additivity of the slope in the η_{sp}/C vs. C plot of the polyblends, PVC-poly(MMA) and PVC-poly(GMA), between theoretical and experimental values. The results show that the additivity of the slope in the reduced viscosities vs. concentration for the compatible blend, PVC-poly(MMA), is better than that for the incompatible blend, PVC-poly(GMA). The additivity law of the slope in the plot of the reduced viscosity vs. concentration in a blend can be simply given by

$$S_{\text{blend}} = X_1 S_1 + X_2 S_2 \quad (8)$$

where X_1 and X_2 are the weight percentage polymers 1 and 2, respectively; S_1 and S_2 are the slopes in the reduced viscosity versus polymer concentration plot for polymers 1 and 2, respectively.

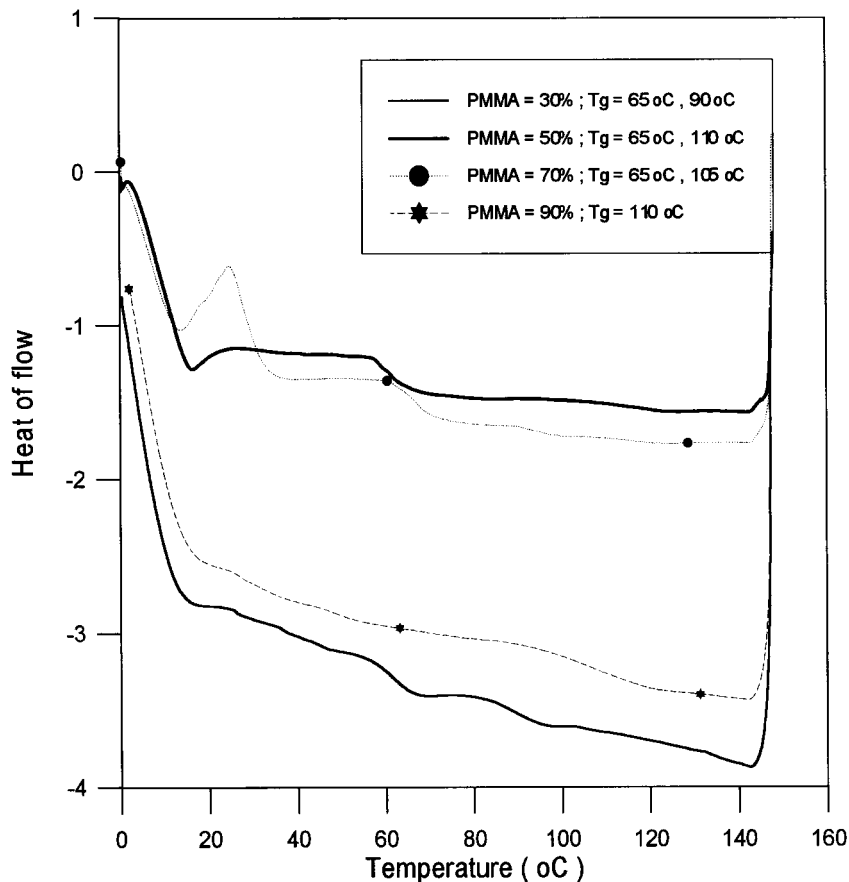


Figure 13 DSC curves for poly(GMA)/poly(MMA) polymer blends.

The results shown in Figures 4 and 5 indicate that the compatibility of the polymer pairs depends on the additivity of the slope in the reduced viscosity vs. polymer concentration for the respective polymer. At the same time, we found that the tendency of the deviation (D) of slopes deviated from additivity law is similar to the tendency of the change of heat of mixing (ΔH_m). Hence, the deviation of the slope deviated from additivity law and ΔH_m for respective polymer pairs against the composition of various polyblends are plotted in Figures 6–10 for PVC–poly(MMA), PVC–poly(GMA), PVC–PS, and poly(MMA)–poly(GMA) blend systems, respectively. Contrasting the D value and ΔH_m from Figures 6–10, it is noted that the deviations of slope's additivity at 15% are similar to the heat of mixing at 10×10^{-3} cal/mol. This occurrence implies that the compatible blend can be judged, while the deviation of slope's additivity is smaller than 15%.

The comparative values of the compatible range for a polyblend estimated from thermodynamic method (ΔH_m) and viscometric method are

shown in the Table II. The data shown in Table II indicate that the compatible ranges estimated by thermodynamic methods are almost identical to those obtained from viscometric method. Re-stated, this D value can be used to judge the compatibility of various polymer blends.

The D value for a blend can be given as follows:

$$D(\%) = \frac{|S_{\text{the}} - S_{\text{exp}}|}{|S_{\text{the}}|} \times 100\% \quad (9)$$

where S_{the} is a theoretical slope obtained from the additivity law of slope in the reduced viscosity vs. concentration for two homopolymers according to eq. (8). S_{exp} is a slope obtained from experiment according to Huggin's equation, eq. (2).

Improvement of Incompatible Blend System by Grafted Copolymer (Compatibilization Agent Test)

The preparation of PVC-*g*-GMA grafted copolymer was reported in our previous article.¹⁹ The

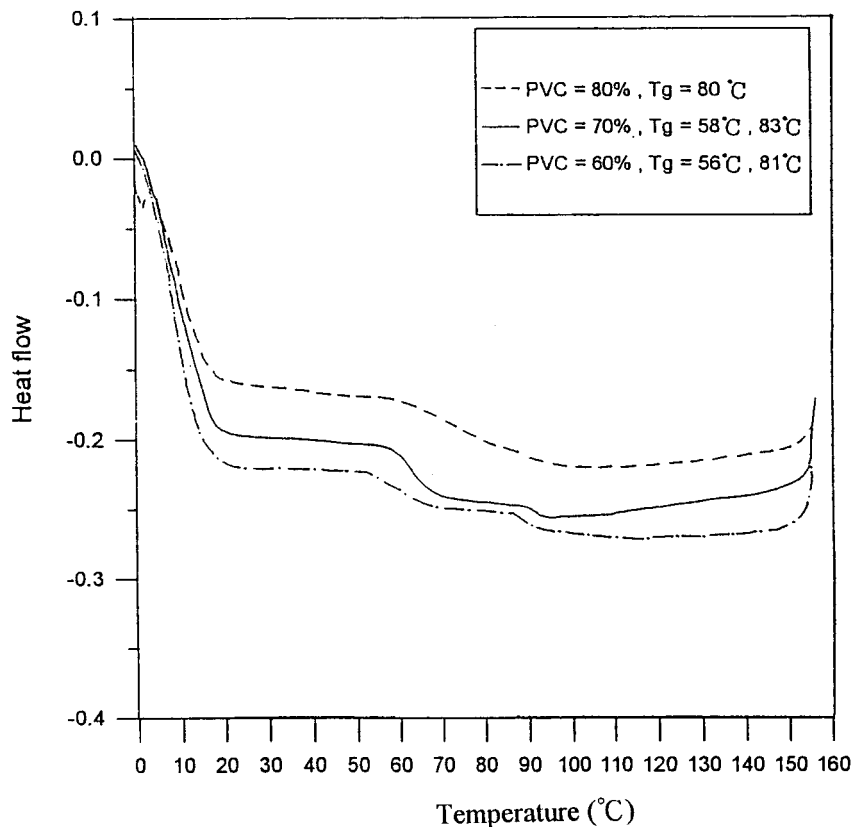


Figure 14 DSC curves for PVC-poly(GMA) polymer blends.

influence of various conditions, such as monomer concentration, polymerization temperature, degree of dehydrochlorinated of PVC, etc., on the percentage of grafting has been investigated. It is always interesting for us to study the functional monomer such as GMA or HEMA grafted onto the PVC. From above-mentioned results, the narrow compatible range of PVC and poly(GMA) blend was found. Hence, the PVC-*g*-GMA grafted copolymer is used as compatibilization agent for PVC-poly(GMA) blend to improve the compatibility of this polymer-polymer pair and to check the suitability of the additivity law of slope in reduced viscosity method.

0.5 g of 60 wt % PVC and 40 wt % poly(GMA) incompatible blend system is therefore chosen, and 16.68% grafting percentage of PVC-*g*-GMA copolymer with various weights was added as a compatibilization agent to measure their reduced viscosities.

The *D* value in the blend was obtained according to eq. (9). Figure 11 shows the *D* value versus the weight fraction of the added grafted copolymer.

The result shown in Figure 11 indicates that

the 38% *D* value for the incompatible blend [60 wt % PVC/40 wt % poly(GMA)] would be reduced to less than 15% when the 16.68% grafting of PVC-*g*-GMA (over 0.05 g) was added into that system. This result explicitly indicates that the incompatible blend at this composition would become a compatible blend as long as 10 wt % graft copolymer was added into this incompatible system.

From the above result, the deviation of the slope from the additivity law of slope in the reduced viscosity vs. polymer concentration used to judge the compatibility of homopolymers is feasible. To further check this concept, the T_g was measured by differential scanning calorimetry (DSC) in the following section.

DSC Measurement (T_g Test)

To judge the compatibility of a blend, two methods are reported in many articles and works. One is to observe their morphology by SEM; the other is to use glass transition temperature (T_g) measurement by dynamic thermal analysis (DMA) DSC. Because there is no molecular interaction or re-

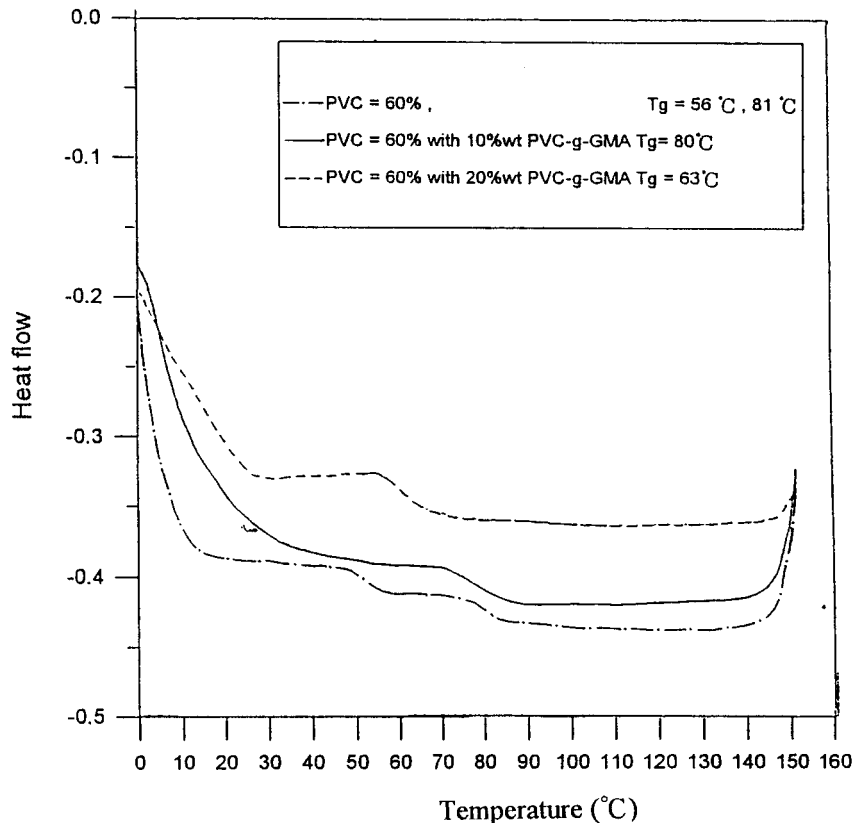


Figure 15 DSC curves for PVC-*g*-GMA added in PVC-poly(GMA) polymer blends.

pulsion in a compatible system, the macromolecules of a blend will sufficiently disperse into each other, and no phase separation will occur in the polymer solution. This phenomenon can be considered as only one polymer in the solution, and only one T_g is observed. However, the incompatible blend would show two T_g s. The T_g for the blend system presented in this article is measured by DSC method. The results of T_g values are shown in Figures 12–14 for PVC-poly(MMA), a compatible blend, and two incompatible blends, PVC-poly(GMA) and poly(MMA)-poly(GMA), respectively.

The data shown in Figure 12 for the PVC-poly(MMA) system exhibit only one T_g in various compositions, but the data shown respectively in Figures 13 and 14 for PVC-poly(GMA) and poly(MMA)-poly(GMA) systems show two T_g s when the weight fraction of PVC is less than 80% and poly(MMA) is less than 90%. These results correspond to the results presented by the reduced viscometric method shown in Figures 6, 7, and 8, respectively. In addition, the incompatible PVC-poly(GMA) blend introduced into some PVC-*g*-GMA graft copolymers as a compatibiliza-

tion agent was also measured by DSC to detect their compatibility. The results shown in Figure 15 exhibit that two T_g points for PVC-poly(GMA) blend were observed, but only one T_g point appears when the PVC-*g*-GMA graft copolymer (16.9% grafting) was added into this blend system over 10 wt %. This result also conforms to the viscometric method presented in this article.

CONCLUSIONS

The additivity law of the slope in the reduced viscosity vs. polymer concentration plot of a blend for two polymers is presented in this article. The absolute deviation range of the additivity of the slope deviated from the slope in the reduced viscosities vs. concentration plot can be used to judge a blend is a compatible or an incompatible blend.

Results obtained from our experiment show that the blends can be considered compatible blends when the absolute deviation range of the slope in the reduced viscosity vs. concentration plot is smaller than 15% for a binary blend system. This phenomenon is further confirmed by

introducing a compatibilization agent into an incompatible blend [PVC–poly(GMA) blends] and further checked by the measurement of T_g for compatible [PVC–poly(MMA)] blends and incompatible [poly(MMA)–poly(GMA)] blends. Hence, using this method, a compatible range for a partly miscible blend can be determined easily, and the needed amount of a compatibilization agent for improving an incompatible blends can be predicted easily.

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