Phase Behavior and Properties of Poly(methyl methacrylate)/Poly(vinyl acetate) Blends Prepared via *In Situ* Polymerization

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ABSTRACT: Polymer blends composed of poly(methyl methacrylate) (PMMA) and poly(vinyl acetate) (PVAc) were prepared via radical-initiated polymerization of methyl methacrylate (MMA) in the presence of PVAc. Differential scanning calorimetry and dynamic mechanical analysis were employed to investigate the miscibility and phase behavior of the blends. The PMMA/PVAc blends of *in situ* polymerization were found to be phase separated and exhibited a two-phase structure, although some chain transferring reaction between the components occurred. The phase separation resulted from the solvent effect of MMA during the *in situ* polymerization, which was confirmed by the investigation of phase behavior based on solution cast blending. Solubility analysis of the polymerized blends indicated that some chain transferring reaction between the components occurred during the polymerization. An abrupt increase in gel content from 21.2 to 72.4 wt % was observed when the inclusion of PVAc increased from 30 to 40 wt %, and the gel component consisted of the component polymers as shown by infrared spectroscopy studies. The thermogravimetric analysis study indicated that the inclusion of a small amount of PVAc gives rise to a marked stabilization effect on the thermal stability. The PMMA/PVAc blends exhibited increased notched impact properties with the inclusion of 5 wt % PVAc. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 69: 675–684, 1998

Key words: polymer blends; phase behavior; methyl methacrylate; poly(methyl methacrylate); poly(vinyl acetate); *in situ* polymerization

INTRODUCTION

Polymer blends have become increasingly important due to their potential for development of new polymer materials because they can possess unusual combinations of properties. The beneficial combinations of polymeric properties usually require appropriate miscibility and phase structure of the polymer blends. From a thermodynamic viewpoint, the miscibility is governed by the nature of the polymer components, such as the intermolecular interactions and the molecular structures, whereas the preparation methods of polymer blends have significant influence on the morphology of the polymer blends[1–5] and in turn affect the properties of the materials. In practice, polymer blends can be prepared via solution and melt mixing, as well as polymerization blending (i.e., *in situ* polymerization blending). Among them, the preparation of polymer blends via *in situ* polymerization was occasionally explored.[6–16] The development of high impact polystyrene (HIPS) might be a successful application of these methods.[6] The study of the phase behavior of *in*

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situ polymerization blends is of importance because the properties of the resulting materials is greatly dependent on phase structure.

The studies of poly(methyl methacrylate) (PMMA) and poly(vinylacetate) (PVAc) blends has provoked the considerable interest of various investigators during the past decades, and the miscibility and the equilibrium phase behavior have long been controversial.[17–28] Singh and Singh[17,18] presented the results of ultrasonic studies in PMMA/PVAc blends prepared from tolenne solution. They found from the linear behavior of the ultrasonic velocity that the blends were compatible within a limited composition range (<70 wt %). Sobliovschi et al.[19,20] pointed out that there was no compatibility in the blends prepared from tetrahydrofuran (THF) when the content of PVAc was lower than 40 wt %; they proposed a so-called "chain pseudo-compatibility" for the PVAc concentration of more that 40 wt %, which showed a maximum at a composition of 80/20 PMMA/PVAc. Using a freeze-drying method, Ichihara and Hatata[20] prepared transparent PMMA/PVAc blends. Differential scanning calorimetry (DSC) studies indicated that the blends showed only a single glass transition. However, after being annealed at 400 K, two glass transitions were detected corresponding to the glass transition of the two pure components. By means of dynamic mechanical analysis (DMA), Jenckel and Herwig[22] carried out refractometric studies of transparent 70/30 and 50/50 PMMA/PVA foils from chloroform solution. In spite of their transparency, two glass transitions corresponding to those of both the components were observed. More recently, Guo[29] restudied the system and concluded that the blends were compatible as evidenced by the appearance of single glass transition temperatures in DSC traces for the blends prepared via chloroform and cyclohexanone cast, and this system possessed the lower critical solution temperature (LCST) of 150°C. However, the blends cast from acetone and THF were phase separated. The phase behavior of the system greatly depends on the method of preparation.

In view of the previous studies, the present studies report the results of our investigation of these blends prepared via radical-initiated *in situ* polymerization of methyl methacrylate (MMA) in the presence of PVAc. The preparation method is quite different from those previously reported. The phase structure and properties of the PMMA/PVAc blends were addressed based on DSC and DMA. The results were compared with those based on solution cast blending to address the effect of a solvent on phase behavior. The structure and chemistry of the resulting blends was examined through solubility measurement and Fourier transform infrared spectroscopy (FTIR). The thermal stability and mechanical properties of the *in situ* polymerization blends was evaluated according to thermogravimetric analysis (TGA) and impact tests, respectively.

EXPERIMENTAL

Materials and Preparation of Samples

The PVAc was kindly supplied by Anhui Vinylon Factory (Anhui, China). It had a quoted number average molecular weight (M_n) of 1.5×10^5. The MMA was reagent grade (Wulian Chemical Factory, Shanghai, China). Prior to use, the inhibitor was removed through washing with 5 wt % NaOH solution, and then the monomer was distilled and further dried with anhydrous Na_2SO_4.

PMMA was prepared by radical-initiated bulk polymerization. The PMMA/PVAc blends were prepared via *in situ* polymerization of MMA in the presence of PVAc; blends with of 95/5, 90/10, 80/20, 70/30, and 60/40 (wt) composition were obtained. A 0.1 wt % of benzoyl peroxide was used as the initiator with respect to the MMA weight. The multistage polymerization process was used. First, the prepolymerization of MMA was conducted at 80°C with continuous stirring for 30 min to avoid the Trommsdroff–Norrish phenomenon and to attain a critical viscosity level; then the solution obtained was cooled down and poured into a mold, which consisted of two polished glass plates separated by Teflon spacers at the four corners and sealed by adhesive tape. The mold was kept in an oven successively at 40°C for 20 h, 80°C for 4 h, and 100°C for 4 h to complete the polymerization reaction. The PMMA so obtained had an M_n of 685,700 and a weight average molecular weight (M_w) of 944,500, which was determined by gel permeation chromatography (GPC) relative to standard polystyrene.

To investigate the reliance of phase behavior on solvents, the 80/20 *in situ* polymerized blend was dissolved using MMA and other solvents, including acetone, THF, chloroform, cyclohexane, dioxane, *N*,*N*-dimethyforamide (DMF), and then cast to prepare the film samples. The majority of the solvents were evaporated at room tempera-

ture (for acetone, THF, and chloroform) or 40°C (for MMA, DMF, cyclohexanone, and dioxane); the residual solvents were removed *in vacuo* at 40°C for 2 weeks.

Measurements

DSC

The calorimetric measurements were made on a Perkin–Elmer DSC-7 differential scanning calorimeter in a dry nitrogen atmosphere. The instrument was calibrated with standard indium. The sample weight used in the DSC cell was kept in the 8–12 mg range. A heating rate of 20°C/min was used in all cases. The midpoint of the slope change of the heat capacity plot was taken as the glass transition temperature (T_g).

The phase separation process was investigated by using DSC. The samples were first annealed at the selected temperature for 10 min and then quenched to −50°C. The heating thermograms were recorded. Then the sample was annealed at the next higher temperature for 10 min and quenched. The higher temperature was changed by 10°C intervals. This procedure was repeated until the occurrence of phase separation was observed. The annealing temperature corresponding to the first change of glass transition was taken as the demixing temperature.

DMA

DMAs were carried out on an Imass Dynastat viscoelastic apparatus in a nitrogen atmosphere, and the temperatures were scanned from 0 to 160°C. The frequency used was 5 Hz, and the heating rate was 3.0°C/min. Specimen dimensions were $6.0 \times 0.4 \times 0.18$ cm.

Solubility Analysis

The solubility behavior of the PMMA/PVAc *in situ* polymerization blends was examined by extracting the samples in chloroform to constant weight. The gel fraction was calculated as the weight ratio of gel to blend.

IR Spectroscopy

A Nicolet 170SX FTIR spectrometer was used to study the structure of the gel. Thin films of the gel extracted from the blends were obtained by directly casting the extracted, wet gel sample onto a NaCl window. After evaporation of most of the solvent in the gel, the films were kept in a vacuum oven at 50°C for 72 h to remove the residual solvent. The specimens of PMMA and PVAc were prepared by casting them from solutions of chloroform onto NaCl windows. All spectra were recorded at room temperature, and a minimum of 32 scans at a resolution of 4 cm^{-1} were signal averaged.

TGA

A Shanghai Apple-II thermal gravimetric analyzer was used to investigate the thermal stability of the blends. The samples (about 10 mg) were heated under an air atmosphere from ambient temperature to 500°C at the heating rate of 10°C/min. The thermal degradation temperature was taken as the onset temperature of the thermal decomposition.

Izod Impact Tests

Izod impact strength measurements were conducted with a Chengde UJ-40 universal impact testing machine at 25°C, and the specimens were prepared according to the standard of ASTM D638. More than five successful determinations were used to obtain the average value.

RESULTS AND DISCUSSION

Phase Behavior of *In Situ* Polymerization Blends

To carry out the polymerization of MMA in the presence of PVAc, solubility between MMA and PVAc is essential. All the MMA/PVAc mixtures in the overall composition were transparent and homogeneous, suggesting that PVAc is totally miscible with MMA. MMA monomer was *in situ* polymerized in the presence of PVAc under the standard conditions after a small amount of initiator was added to the system. As the polymerization proceeded the system gradually became a ternary mixture, which consisted of MMA, PVAc, and newly produced PMMA. At the last stage of the polymerization, MMA monomer was almost totally converted into PMMA; the ternary mixture became the binary PMMA/PVAc polymer blends. It was observed that all initial homogeneous mixtures with various compositions gradually became translucent as the polymerization was carried out, which was in marked contrast with pure PMMA. The change of the clarity implies that the phase separation possibly occurred during the *in situ* polymerization process. To examine the

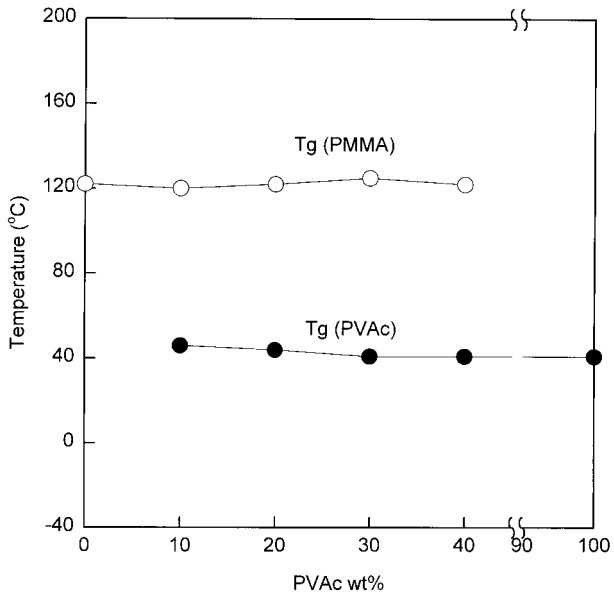

Figure 1 Plot of T_g as a function of PVAc concentration for the PMMA/PVAc *in situ* polymerization blends.

phase behavior, the obtained blends were subject to DSC and DMA measurements. All the DSC curves of the first scan of the *in situ* polymerization PMMA/PVAc blends displayed two separate T_gs as shown in Figure 1. The glass transition at ca. 120°C was ascribed to the PMMA-rich phase, whereas that at ca. 40°C was ascribed to the PVAc-rich phase. The existence of two T_gs indicates that the blends were phase separated. Figure 1 shows that the T_gs of the PMMA-rich phases remained invariant, while those of the PVAc-rich phases slightly increased with increasing PMMA concentration. Figure 2 shows dynamic mechanical properties of the polymerized PMMA, as well as the 90/10 and 80/20 PMMA/PVAc *in situ* polymerization blends. The dynamic mechanical spectrum of the polymerized PMMA [Fig. 2(a)] exhibits a well-defined peak centered at 125°C on the loss modulus E'' versus temperature curve, which was ascribed to its glass transition. The dynamic mechanical spectrum of the 90/10 [Fig. 2(b)] PMMA/PVAc *in situ* polymerization blends clearly displays two maxima at 65 and 114°C on the E'' versus T curve, which correspond to the T_gs of the PVAc-rich phase and the PMMA-rich phase, respectively. The dynamic mechanical spectrum of the 80/20 [Fig. 2(c)] PMMA/PVAc *in situ* polymerization blends shows only one maximum at 54°C on the E'' versus T curve, which was attributed to the T_g of the PVAc-rich phase. However, Figure 2(c) also shows that a shoulder exists at the high temperature side of the E'' versus T curve, which was responsible for the T_g of the PMMA-rich phase. The value for this T_g is estimated to be 110°C from the shoulder. The DMA results presented here were in a good agreement with those of DSC, which further indicated that the PMMA/PVAc *in situ* polymerization blends had a two-phase structure.

The formation of the phase-separation structure does not necessarily indicate the immiscibility of PMMA/PVAc because the "solvent effect" can affect the phase behavior of the blends. As is well known, the solvent effect can affect the phase behavior in some polymer blends prepared via solution casting.[30–36] In the reactive system MMA acts as a reactant, and in the meantime it is also a cosolvent of PVAc and PMMA. Therefore, the solvent effect of MMA could significantly affect the phase behavior of the *in situ* polymerization blends. To confirm this effect, we investigated the phase behavior of the PMMA/PVAc blends prepared through solution casting from various solvents involving MMA, acetone, THF, chloroform, cyclohexane, dioxane, and DMF. The polymerized 80/20 PMMA/PVAc blend was dissolved using the above solvents and the films were cast. Table I summarizes the results of clarity and glass transition properties. The films cast from MMA, acetone, dioxane, and DMF were cloudy; those from chloroform, cyclohexanone, and THF were clear. The DSC studies showed that all the transparent samples exhibited single glass transition temperatures intermediate between those of the plain components, indicating the blends were miscible. When heated to a higher temperature, all these transparent samples became cloudy. The demixing temperatures were determined on the basis of the DSC measurements. A series of thermograms of the 80/20 PMMA/PVAc blends cast from chloroform were representatively shown in Figure 3 after annealed at temperatures between 120 and 160°C and then quenched to −50°C. It is observed that the glass transition of the blends became broad after the blends was annealed at 140°C. The width of the glass transition may reflect the magnitude of local compositional fluctuations in the polymer blends, implying the relative homogeneity or miscibility of the system. When further annealed at the higher temperature, the splitting of the glass transition was observed, suggesting the occurrence of phase separation. The demixing temperatures of the blends cast from chloroform, THF, and cyclohexanone are identical; these could be governed by the equilibrium phase behavior

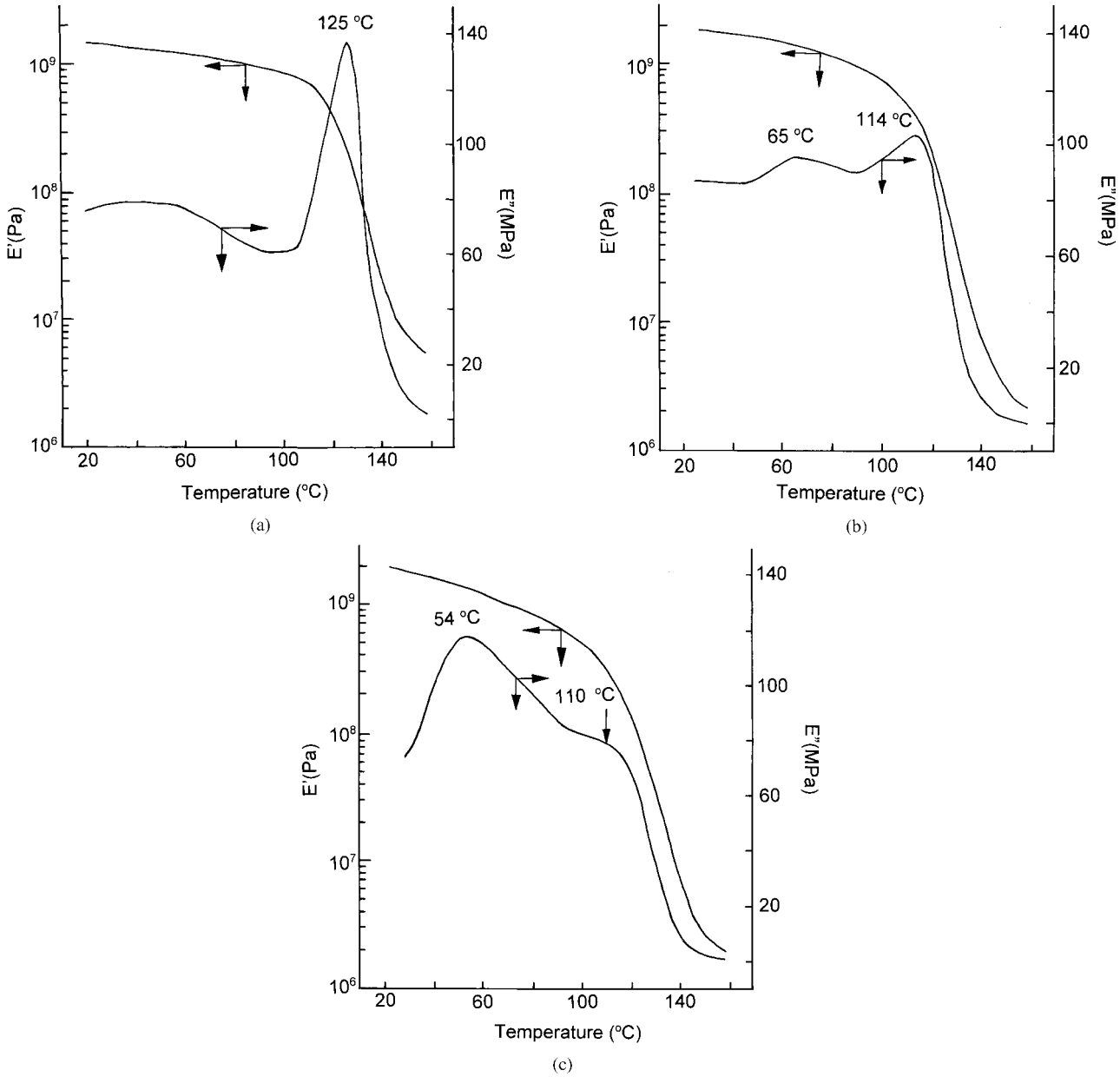

Figure 2 Dynamic mechanical spectra of (a) polymerized PMMA and (b) 90/10 and (c) 80/20 PMMA/PVAc *in situ* polymerized blends.

of the blends. On the other hand, all the cloudy samples gave the two separate glass transition temperatures, suggesting the MMA blends were phase separated. Shown in Figure 4 are the DSC thermograms of the sample of the film cast from MMA; the two separate glass transitions centered at ca. 40 and 110°C are clearly displayed. In the first DSC traces, the appearance of an enthalpy relaxation peak close to the glass transition of the PMMA-rich phase was responsible for the aging below the T_g for a long time. In terms of the above results, it is believable that the formation of phase separation in the *in situ* polymerization process is due to the solvent effect of MMA. The solvent effect on the homogeneity of casting polymer blend films has previously been interpreted in terms of the difference in the two polymer–solvent interaction parameters $|\chi_{12} - \chi_{13}|$ or $|\Delta\chi|$ [subscript 1 refers to solvent and subscript 2 (or 3) stands for polymer]. From a ternary phase dia-

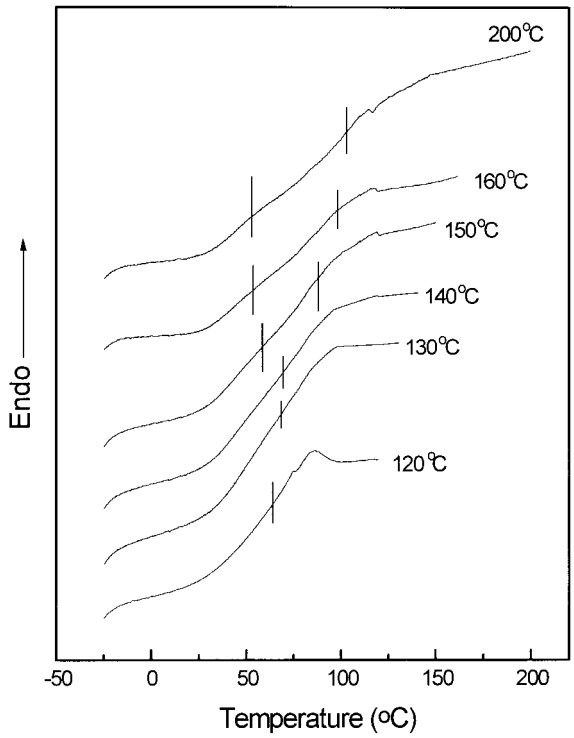

Figure 3 DSC thermograms of 80/20 PMMA/PVAc blends cast from chloroform and annealed at various temperatures for 10 min.

gram, a homogeneous system is attained only with a suitably small $|\Delta\chi|$ in addition to the necessary requirement of a very small polymer–polymer interaction parameter χ_{23}.[35] In the present case, χ_{23} was calculated to be -4.3×10^{-4} according to the LCST phase diagram obtained in the previous work.[29] The χ_{12} and χ_{13} were 0.41 and 0.48, respectively, which were estimated through the solubility parameters[36]; thus, $|\Delta\chi|$

Table I Clarity and Calorimetric Results of Casting Films of Polymerized 80/20 (wt) Blends

Solvents	Clarity	T_g (°C)		Demixing Temp. (°C)
Methyl methacrylate	Cloudy	38	95	
Acetone	Cloudy	40	90	
Tetrahydrofuran	Clear	75		145
Chloroform	Clear	74		145
Cyclohexanone	Clear	70		145
N,*N*-Dimethylforamide	Cloudy	40	90	
Dioxane	Cloudy	40	90	

[a] From the first DSC trace.

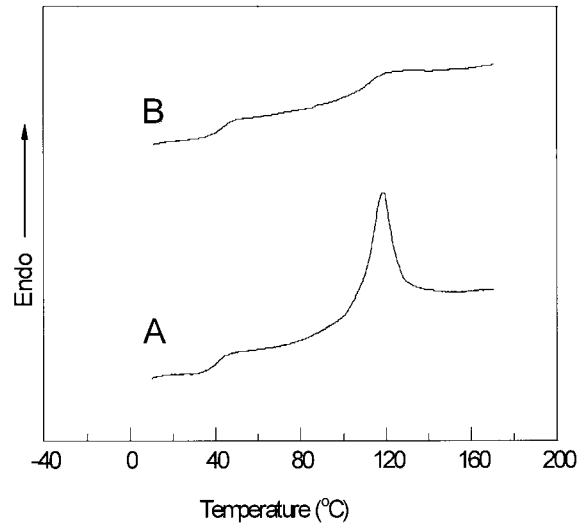

Figure 4 The DSC thermograms of 80/20 PMMA/PVAc blends cast from MMA.

was 0.07. In addition, it should be pointed out that, in the present case, the highest temperature of polymerization was 100°C, which is lower than the LCST temperature (150°C) of PMMA/PVAc blends[29]; hence, it is impossible for the temperature to give rise to the phase separation.

From kinetics of phase separation viewpoint, the formation of a phase-separated structure can be interpreted as demixing induced by polymerization. Inoe et al.[36–40] and Flory[41] proposed that the phase separation induced by polymerization underwent spinodal decomposition. The present result is similar to that for the PMMA/poly(ethylene-*co*-vinyl acetate) (EVA) *in situ* polymerization blends reported by Chen et al.[14] They investigated the structural development during radical polymerization of a mixture of MMA and EVA by light scattering and optical microscopy.

Solubility Behavior

PMMA/PVAc *in situ* polymerization blends with PVAc contents of up to 20 wt % were completely soluble in acetone, chloroform, etc. However, the blends containing 30 and 40 wt % PVAc were not completely soluble in common solvents and some insoluble products existed. It is evident that the gel formed during the *in situ* preparation of the blends. To examine the gelation behavior, the blends were extracted in chloroform for 72 h. The gel fraction was calculated as the weight ratio of the gel to the blend, and the values of gel fraction

Table II Gel Fraction of PMMA/PVAc In Situ Polymerization Blends

	PVAc Content (wt %)					
	0	5	10	20	30	40
Gel fraction (wt %)	—	—	—	—	21.2	72.4

thus obtained are listed in Table II. It is noted that the values of the gel fraction for the blends containing 30 and 40 wt % PVAc were 21.2 and 72.4 wt %, respectively. This result clearly indicates that a grafting reaction and/or crosslinking occurred during polymerization.

Figure 5 shows FTIR spectra of PVAc, PMMA, and the gel extracted from the 60/40 PMMA/PVAc *in situ* polymerization blend. The figure shows that the difference between the two pure polymers in the fingerprint region (650–1500 cm^{-1}) is distinguishable, although there are similar functional groups for the two polymers. The spectrum of the gel is very like that of PMMA, implying that the gel consists of a major PMMA component. However, the figure shows that several new bands appear that are assigned to PVAc. These bands are at 1250, 1025, 950, and 606 cm^{-1} as indicated in the figure. This result shows that PVAc macromolecules grafted onto the PMMA network in the gel exist. Actually, MMA monomer can graft onto PVAc macromolecules via chain transfer reactions during *in situ* polymerization.

The chemical reaction in monomer/polymer systems is rather complicated because it may involve chain extension, branching, grafting, and crosslinking. The present system involves the radical polymerization of MMA in the presence of PVAc; the reaction is only the polymerization of MMA to form PMMA and hence to form PMMA/PVAc *in situ* polymerization blends. In the absence of chain transfer, the growth of PMMA chains occurs by a fast chain growth process. Both the rate of polymerization R_p and the kinetic chain length DPv (hence, the molecular weight) increase with the increase of MMA monomer concentration as suggested by eqs. (1) and (2)[41,42]:

$$R_p = K_p(K_d/K_t)^{1/2}[I]^{1/2}[\mathrm{MMA}] \quad (1)$$

$$\mathrm{DPv} = R_p/R_i = K_p[\mathrm{MMA}]/\{2(K_d)^{1/2}(K_t)^{1/2}[I]^{1/2}\} \quad (2)$$

where K_d, K_p, and K_t are the rate constants of decomposition of initiator, propagation, and termination, respectively; (I) and [MMA] represent the molar concentration of initiator and MMA, respectively; and $R_i = 2K_d[I]$ is the rate of initiation. However, because the preliminary MMA polymerization takes place in the presence of PVAc, there is a possibility of chain transfer.[43,44] This helps in reducing the kinetic chain length DP, as

$$1/\mathrm{DP} = 1/\mathrm{DPv} + C_E[\mathrm{PVAc}]/[\mathrm{MMA}] \quad (3)$$

where C_E represents the chain transfer constant to PVAc whose concentration is [PVAc]. It can be seen from eq. (3) that an increase in PVAc content will result in a reduction in the kinetic chain length and hence the molecular weight of PMMA formed. This means that the chain transfer process will become predominate with an increase of PVAc concentration. As a result, the chain transfer results in grafting and crosslinking and thus the gel formation. Gelation occurs due to the *in situ* formation of the graft copolymer and/or cross-

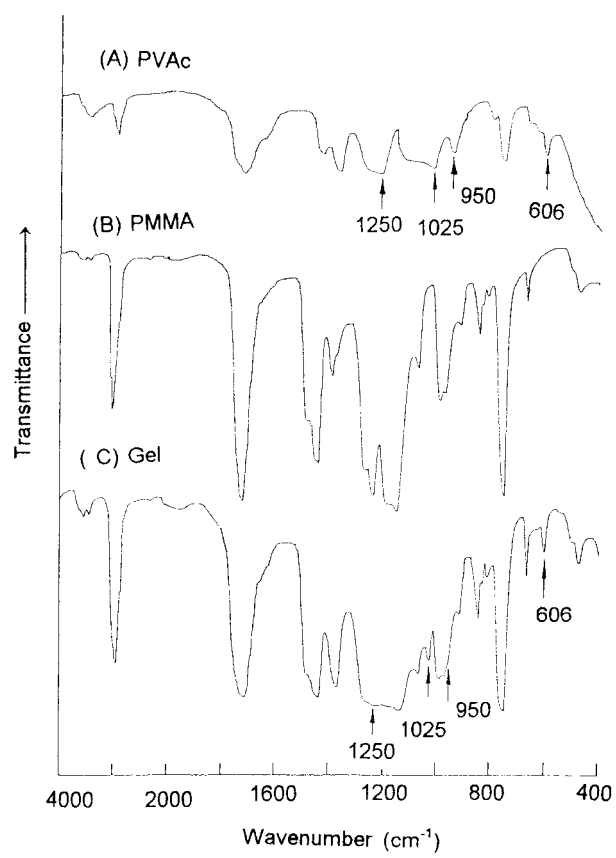

Figure 5 FTIR spectra of PVAc, PMMA, and the gel extracted from the 60/40 PMMA/PVAc *in situ* polymerization blend.

linking products during polymerization. It should be pointed out that the abrupt increase in gel content (from 21.2 to 72.4 wt % going from 30 to 40 wt % PVAc, as shown in Table II) is rather dramatic and surprising. As is known, the chain transfer reaction results in the appearance of a large number of radicals on the molecule backbone. Each backbone radical can act as a reacting center at which MMA monomer can polymerize and graft onto PVAc macromolecules, or these radicals recombine with each other or further undergo new chain transfer reaction. In such case, many new polymer chains grow from the matrix chain. This reaction has phenomenally been described as "template polymerization" (or "matrix polymerization"); an abrupt increase in unsolubles was observed for a threshold value of the matrix polymer.[45] In the PVAc/MMA mixtures, chain transfer radicals increase with an increase of the PVAc concentration. At the vicinity of the gel point, the polyradical chains start to appear and accumulate in a rather sudden manner.[46] Therefore, a large amount of gel and crosslinking product was formed.

Thermal Stability and Impact Property

To investigate the thermal stability of the blends, TGA was used to measure the onset degradation temperature ($T_{d,\text{onset}}$) of the blends in air. Figure 6 summarizes the values of $T_{d,\text{onset}}$ as a function of blend composition for PMMA/PVAc *in situ* polymerization blends. It can be seen from the figure that $T_{d,\text{onset}}$ was increased by the incorporation of PVAc up to 5 wt %, then it modestly decreases with PVAc content. The $T_{d,\text{onset}}$ shows a maximum at 5 wt % PVAc. For all the blends, the values of the $T_{d,\text{onset}}$ are higher than that of pure PMMA and the presence of PVAc slightly improves the thermal stability of PMMA. This phenomenon could be attributed to the synergistic contribution of the two phases in energy transportation. The degradation of the components was also observed in other PMMA blends by other authors.[47–50]

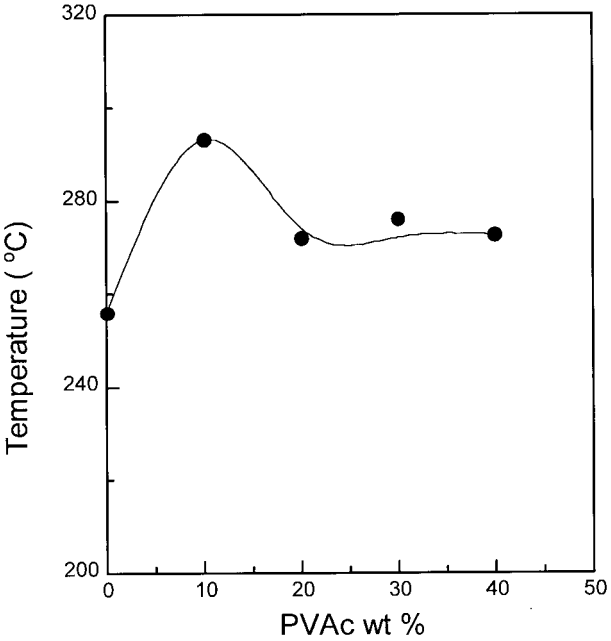

Figure 6 Onset degradation temperature as a function of blend composition for PMMA/PVAc *in situ* polymerization blends. The blends were heated at 10°C/min in air.

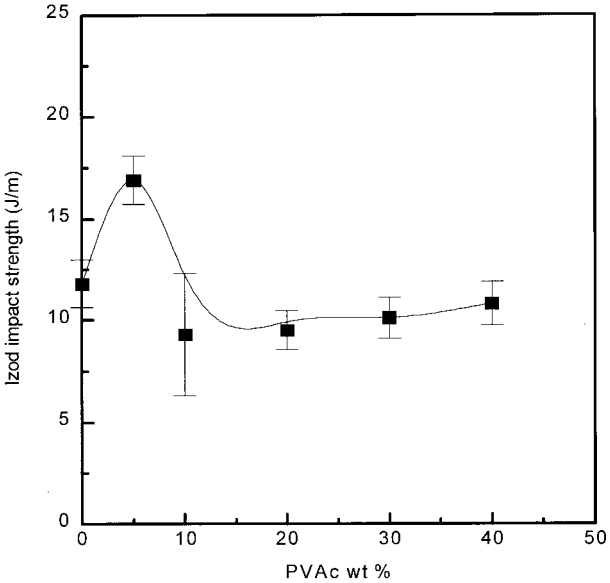

Figure 7 Izod impact strength of the PMMA/PVAc *in situ* polymerization blends.

Figure 7 shows the Izod impact strength of PMMA/PVAc *in situ* polymerization blends as a function of PVAc content. The 95/5 PMMA/PVAc *in situ* polymerization blend has a higher impact strength than that of pure PMMA. Kojima et al.[15] reported that PMMA can be toughened by elastomeric materials and EVA through radical-initiated *in situ* polymerization of MMA in the presence of EVA. However, it is noticeable that in the present case the brittle PMMA was toughened by a small amount of brittle materials and PVAc via the *in situ* polymerization method.

CONCLUSIONS

Polymer blends composed of PMMA and PVAc were prepared via radical-initiated polymeriza-

tion of MMA in the presence of PVAc. DSC, DMA, and scanning electronic microscopy were employed to investigate the miscibility and phase behavior of the blends. The PMMA/PVAc blends of *in situ* polymerization were found to be phase separated and exhibited a two-phase structure, although some chain transferring reaction between both components occurred during the polymerization as evidenced by the solubility experiment and FTIR studies. The phase separation is believed to have resulted from the solvent effect of MMA during the *in situ* polymerization. The TGA study indicated that the inclusion of 10 wt % PVAc resulted in a substantial stabilization effect. The PMMA/PVAc blends exhibited increased impact properties with the inclusion of 5 wt % PVAc, which was expressed by notched impact strength.

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