

Polymer-Polymer Miscibility and Enthalpy Relaxations

Martin Bosma, Gerrit ten Brinke,* and Thomas S. Ellis†

Department of Polymer Chemistry, State University of Groningen, Nijenborgh 16, 9747 AG Groningen, The Netherlands. Received September 14, 1987

ABSTRACT: Annealing of polymers below the glass transition temperature results in a decrease in enthalpy that is recovered during heating. The enthalpy recovery is visible as an endothermic peak in a differential scanning calorimetry (DSC) scan. The position of this peak depends on the thermal treatment given and on the structure of the material itself. Because different polymers behave differently, the phenomenon can be utilized to investigate polymer-polymer miscibility of polymers with similar T_g values. Therefore, by annealing the blends at the temperature of interest and subsequent sub- T_g annealing, one can monitor phase behavior resulting from the initial treatment by inspection of the enthalpy recovery. Two systems were investigated to illustrate this: an immiscible blend of poly(vinyl chloride) and poly(isopropyl methacrylate) and a miscible blend of poly(vinyl chloride) and poly(methyl methacrylate).

Introduction

In recent publications^{1,2} it was shown that the value of binary interaction parameters between polymers can be found from simple experimental procedures involving differential scanning calorimetry. An essential element to these studies is the availability of a complete set of different yet complementary polymers. This can best be illustrated by the following example. The collection of polymers poly(2,6-dimethyl-1,4-phenylene oxide) (PPO), polystyrene (PS), random copolymers of styrene and *o*-chlorostyrene (P(S-*o*ClS)), random copolymers of styrene and *p*-chlorostyrene (P(S-*p*ClS)), and random copolymers of *o*-chlorostyrene and *p*-chlorostyrene (P(*o*ClS-*p*ClS)) contain four different monomers. The phase behavior of all possible binary mixtures is therefore determined by six different binary interaction parameters. Given an appropriate molecular weight range, it is possible to find copolymer compositions for which at a given temperature ($\geq 200^\circ\text{C}$) there is a lower critical solution temperature (LCST) for any of the following blends: PPO/P(*o*ClS-*p*ClS), PS/P(*o*ClS-*p*ClS), PPO/P(S-*o*ClS), and PPO/P(S-*p*ClS). For the first two systems there are two different copolymer compositions where an LCST can be found. Hence, as pointed out in ref 1, six linear equations involving six interaction parameters can be established, and their values determined as a function of temperature.

Another series of polymers suitable for this type of analysis is obtained by replacing the chlorine atom by a fluorine atom. However, one of the attractive features of the former case is lost because of the close proximity of the respective T_g values of the polymers obtained. The phase behavior is often most conveniently determined by calorimetric measurements using the well-known single glass transition temperature (T_g) criterion. The onset of phase separation in blends that are miscible at a particular temperature is located by annealing at various temperatures above T_g , followed by a rapid quench to ambient temperature and subsequent thermal analysis at 10 or 20 $^\circ\text{C}/\text{min}$. This measurement when performed by DSC then reveals either one or two discontinuities in the heat capacity, according to whether or not phase separation has taken place. Clearly, this procedure only works if the T_g values of the pure components are sufficiently far apart. This happened to be the case for the chlorinated styrene polymers but ceased to be true once chlorine was replaced by fluorine. PS, P(S-*o*FS), P(S-*p*FS), and P(*o*FS-*p*FS) all have T_g values around 100°C .

Therefore, a principal objective of this article is to demonstrate that contrary to generally accepted opinions,³

calorimetric methods remain a valid experimental technique to establish polymer-polymer phase behavior even when the T_g of the constituent polymers are very close to each other. The procedure relies on the phenomenon of enthalpy recovery in physically aged glassy blends. In principle the phase behavior of a blend following a thermal treatment can be evaluated by annealing at temperatures below T_g followed by DSC analysis in the usual manner. Physical aging of polymer blends has received some attention in the past;^{4,5} however, we believe this article to show the first instance of its use to establish polymer-polymer phase behavior.

Annealing of polymers below the glass transition temperature results in a relaxation toward equilibrium and a corresponding decrease in thermodynamic quantities such as enthalpy and volume. The relaxation process is a subject extensively studied in recent years experimentally as well as theoretically (see ref 6-13 and references therein). Various related approaches are available. Here we will restrict ourselves to a short overview of Moynihan's⁹ description. This model was also adopted by Hodge et al.¹³⁻¹⁶ in their calculations of the effects of aging on sub- T_g endotherms. From an initial temperature T_0 where the sample exhibits virtually instantaneous relaxations, it is cooled fast to a temperature T_a in the glassy regime. After an annealing time t_a a DSC scan is taken. During annealing, the relaxation toward equilibrium of the enthalpy H is described by a relaxation function $\Phi(t)$ defined by

$$\Phi(t) = (H(t) - H(\infty)) / (H(0) - H(\infty)) \quad (1)$$

where $H(\infty)$ is the equilibrium value of the enthalpy at T_a . The relaxation function is taken to be of the Williams-Watts form:

$$\Phi(t) = \exp(-(t/\tau)^\beta) \quad (2)$$

where $0 < \beta \leq 1$ is a measure of the width of the relaxation spectrum and τ is given by¹⁷

$$\tau = A \exp[x\Delta h/RT + (1-x)\Delta h/RT_f] \quad (3)$$

In eq 3, A is a fitting constant, R the gas constant, $0 < x \leq 1$ a nonlinearity parameter introduced by Moynihan et al.,³⁶ Δh an activation enthalpy, and T_f the fictive temperature at which the equilibrium value of the enthalpy is given by $H(t)$. The notion of a fictive temperature T_f was first introduced by Tool.¹⁸ The decrease in enthalpy is recovered during reheating and is characterized by an endothermic peak in the heat capacity at temperatures ranging from well below to the upper edge of the glass transition temperature. The actual position is determined by a number of factors, some of which can be varied, such as cooling rate, aging temperature, aging time, and heating rate, and others that are characteristic for the material investigated, such as A , Δh , x , and β . The first theoretical

† Present address: Polymers Department, General Motors Research Labs, Warren, MI 48090-9055.

Table I
Molecular Weights and Glass Transition Temperatures

material	M_w	M_n	T_g , °C
PVC	60 000	33 000	80.2
PMMA	100 000	45 000	110.0
PiPMA	170 000	48 000	82.5

prediction of a sub- T_g endotherm was made by Kovacs et al.⁸

The fact that each polymer has its own specific aging behavior, manifested in the position and magnitude of the enthalpy recovery peak, can be used to determine polymer-polymer miscibility when the polymers in question have a similar glass transition temperature. Two different but related systems have been investigated to demonstrate this. The first system consists of poly(vinyl chloride) (PVC) and poly(isopropyl methacrylate) (PiPMA). These polymers have nearly identical glass transition temperatures, and there are some indications¹⁹ that PVC and PiPMA are immiscible. Clearly, the single T_g criterion is of no use. However, physical aging of blends of PVC and PiPMA gives, as will be shown, rise to two separate enthalpy recovery peaks, thereby demonstrating the presence of two different phases. The second system consists of PVC and atactic poly(methyl methacrylate) (PMMA), polymers that are known to be miscible for suitable chosen molecular weights.²⁰ Furthermore, the T_g values are sufficiently far apart to demonstrate miscibility by using the conventional single T_g criterion. Physically aged blends of PVC and PMMA show, as will be demonstrated, a single enthalpy recovery peak with all the characteristics of enthalpy recovery peaks of a pure polymer. The choice of polymers was also motivated by the fact that PVC and PMMA were known to behave quite differently with respect to aging.²¹⁻²³ But we will argue that a similar but more subtle approach will also work if the difference in aging behavior is less pronounced.

Experimental Section

All three materials were commercially available products. Poly(vinyl chloride) was obtained from P  chiney et St. Gobain (Lucovyl RB 8010), atactic poly(methyl methacrylate) from ICI (Diakon MO 900), and atactic poly(isopropyl methacrylate) from Polysciences. All polymers were purified by a precipitation procedure and dried under vacuum at 50 °C for at least 1 week. The molecular weights were determined by gel permeation chromatography (Waters alc/gpc 150 c) using tetrahydrofuran (THF) as an eluent. Values of M_w and M_n were calculated relative to polystyrene standards. Thermal analysis was performed with a Perkin-Elmer differential scanning calorimeter (DSC-7) with a heating rate of 20 °C/min. The onset glass transition temperature was measured as the point of intersection of the extrapolated baseline with a line drawn through the point of inflection of the incremental change in heat capacity. Onset T_g values and molecular weights are shown in Table I. Blends of PVC and PiPMA and PVC and PMMA were obtained by coprecipitation from dilute THF solutions (2.5 wt %) into a large excess of petroleum ether. The composition of each blend was 50/50 wt %.

Samples prepared for aging were kept at a temperature $T_0 > T_g$ for 5 min to erase previous history. In most cases $T_0 = 160$ °C, except for one series of experiments where $T_0 = 195$ °C. The samples were then cooled by quenching in liquid nitrogen followed by annealing for different amounts of time t_a at $T_a < T_g$. Usually $T_a = 60$ °C. Subsequently, a DSC scan was taken from -5 to 160 °C. Finally, after being annealed at 160 °C for 5 min, the samples were quickly cooled to -5 °C, and a second scan was taken. In all cases, the sample size was approximately 18 mg.

Results and Discussion

Figures 1 and 2 show thermograms of PVC and PiPMA aged at 60 °C for the amounts of time indicated. The

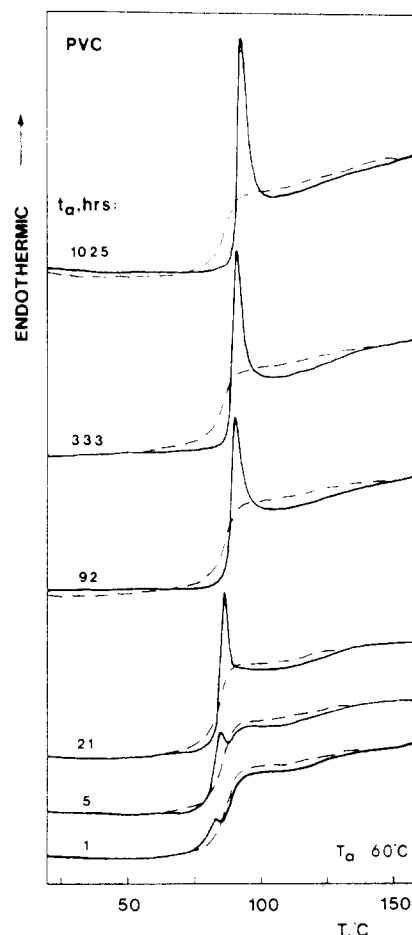


Figure 1. Thermograms of PVC, quenched from 160 °C and aged at 60 °C for the indicated times: first scan (—); second scan (---).

presence of a pronounced endothermic peak, whose position and magnitude generally increased with increasing aging time, t_a , is a well-established feature of physical aging. The dashed lines correspond to the conventional scans taken after the physical aging had been erased. Similar results for PVC were obtained before by Illers,²¹ Gray and Gilbert,²⁴ and Berens and Hodge.²⁵ For PiPMA, the only information available is due to Yoshida and Kobayashi,²⁶ who studied the effect of the size of the side group of poly(alkyl methacrylates) on the rate of relaxation. They concluded that the relaxation time became longer for a larger side group. Endothermic heat capacity peaks for PMMA have also been observed by various investigators.^{4,11,23} Since for the present study quantitative results for PMMA are not required, this polymer was not investigated in close detail.

Here our main concern is the position of the maximum, T_{max} , and the onset, T_{ons} , of the enthalpy recovery peaks of PVC and PiPMA as a function of annealing time t_a . Both T_{max} and T_{ons} are known to be approximately proportional to $\log t_a$ for a given annealing temperature T_a . As far as T_{ons} is concerned, this fact was first emphasized by Ellis and Karasz²⁷ in a study on enthalpy recovery in network epoxy/water systems. Figure 3 shows T_{max} of PVC and PiPMA as well as T_{ons} of PVC as a function of $\log t_a$. Careful inspection of T_{max} reveals a considerable difference between both polymers. For a given annealing time the position of the peak is at a much lower temperature for PVC than for PiPMA, despite their nearly identical glass transition temperatures (Table I). It should be remembered, however, that the temperature interval $T_g - T_a$ is slightly different, which may also be expected to influence aging kinetics. Accordingly, the difference in

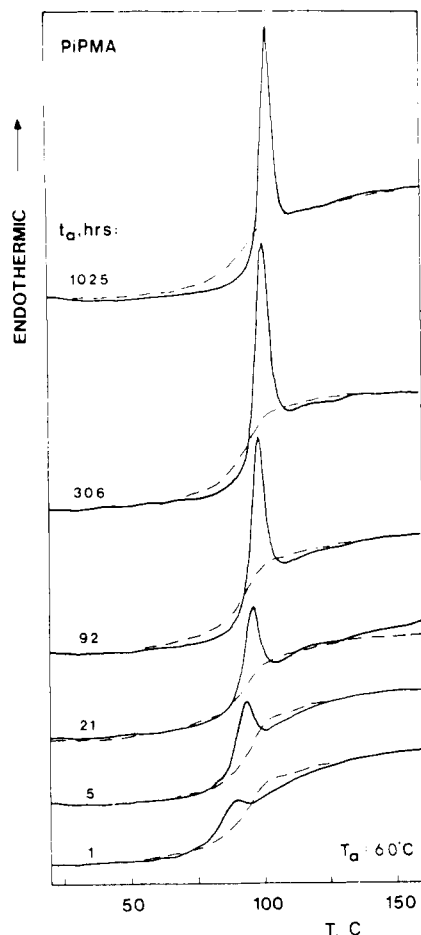


Figure 2. Thermograms of PiPMA, quenched from 160 °C and aged at 60 °C for the indicated times: first scan (—); second scan (---).

behavior cannot be attributed completely to their structural differences.

Berens and Hodge²⁵ investigated the influence of the value of the parameters β , x , and Δh , introduced previously on the position of the enthalpy recovery peaks in their study on the mathematical modeling of the effects of annealing. Smaller values of β , corresponding to increased nonexponentiality or a broader distribution of relaxation times, lead to lower values of T_{\max} . On the other hand, smaller values of the nonlinearity parameter x , which partitions the temperature and structure dependence of the characteristic time τ , lead to increased values of T_{\max} . The effect of decreasing the activation enthalpy Δh is qualitatively the same as decreasing x . As far as values of β , x , and Δh are concerned, nothing is known for PiPMA, but various estimates are available for PVC and PMMA.^{11,14,16} The general conclusion seems to be that in particular the value of β is lower for PVC than for PMMA. Apparently, PVC has a broader spectrum of relaxation times, a feature that may be related to physical cross-linking induced by small amounts of crystallinity.

Blends of PVC/PiPMA and PVC/PMMA were investigated to demonstrate the utility of simple annealing experiments with respect to the assessment of polymer-polymer miscibility. Miscibility of homopolymers requires the presence of specific intermolecular interactions. In the case of PVC and poly(alkyl methacrylates) the specific interaction is of the Lewis acid-base type.²⁸ The carbonyl oxygen of the acrylic polymer behaves as the electron donor, and the α hydrogen of PVC as the electron acceptor. Although this type of interaction will generally be present in these systems, the number of specific interactions at any

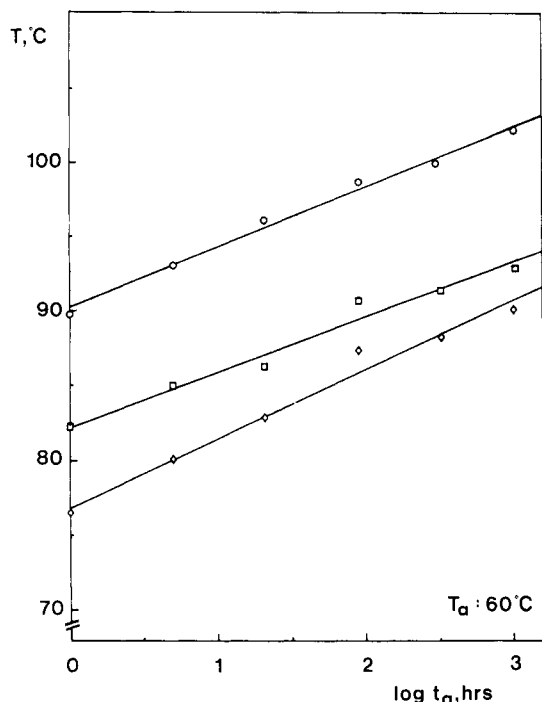


Figure 3. T_{\max} and T_{ons} versus $\log t_a$ for PiPMA and PVC: (○) T_{\max} of PiPMA; (□) T_{\max} of PVC; (◇) T_{ons} of PVC.

given time is in the majority of cases too small and London dispersion forces dominate, resulting in phase separation.²⁹ An exception to this is the PVC/PMMA blend system, which will be considered later.

For PVC/PiPMA, the situation is not clear. Kern¹⁹ noticed that equal weights of PVC and PiPMA dissolved in THF with a total polymer concentration of 15 wt %/vol % underwent phase separation. However, he also observed the same effect using PMMA instead of PiPMA. We know from our own experience that the miscibility of PVC and PMMA is quite delicate. Moreover, a larger side group may affect the miscibility adversely, as is the case for blends of poly(vinylidene fluoride) with PMMA and poly(ethyl methacrylate).^{30,31} Hence, PVC and PiPMA were expected to be immiscible. Blends of PVC and PiPMA were prepared by the well-known precipitation method. The choice of nonsolvent can be very important when using this method, as demonstrated recently by Chiou et al.³² All samples were always annealed at 160 or 195 °C to eliminate the solvent effect and thermal history. If, due to the solvent effect, homogeneous blends were obtained, whereas both components are not miscible in the melt, phase separation will occur during the annealing process. Generally, the most unambiguous criterion of polymer miscibility is the detection of a single glass transition whose temperature is intermediate between those corresponding to the pure components.³³ In our case both components have the same T_g , and the criterion has to be modified.

Figure 4 shows the thermal scans of PVC/PiPMA blends annealed at 160 °C for 5 min and aged at 60 °C for the amounts of time indicated. The solid lines represent the first scans, and the dashed lines the second scans, taken after the physical aging had been erased. The solid lines contain two different enthalpy recovery peaks corresponding to two different phases. The second scans show only one incremental change in specific heat, clearly due to the similar T_g values of PVC and PiPMA. A comparison with the results presented in Figure 3 shows that the enthalpy recovery peak at the lowest temperature, mainly visible as a shoulder, corresponds to the PVC-rich phase.

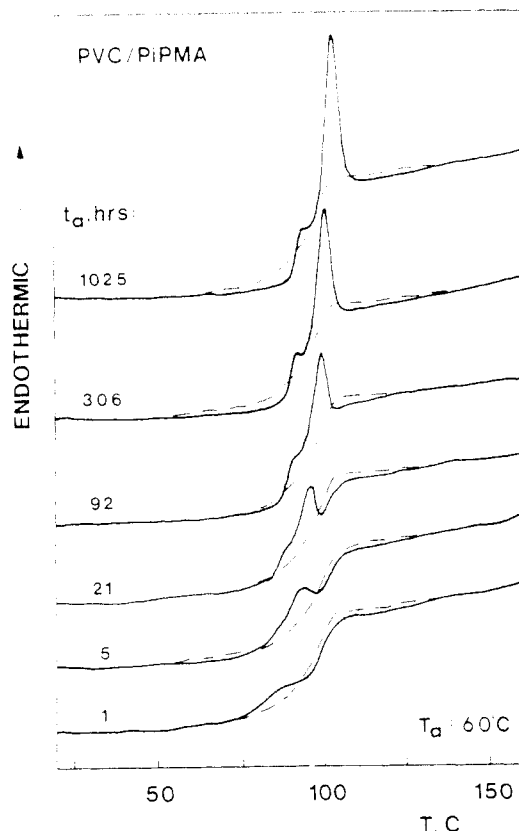


Figure 4. Thermograms of PVC/PiPMA, quenched from 160 °C and aged at 60 °C for the indicated times: first scan (—); second scan (---).

The blends were also annealed at a somewhat higher temperature of 195 °C before aging to enhance the difference between the two enthalpy recovery peaks. Figure 5 shows the results. The difference between the peaks is more pronounced now, however, mainly with respect to magnitude and sharpness. The positions remain, as will become clear, nearly the same. It indicates that the two phases present are better defined now probably due to larger average domain sizes as a result of a somewhat lower viscosity and increased thermodynamic driving force for phase separation. The last statement follows from the argument that the Flory-Huggins parameter χ is most likely an increasing function of temperature, in the temperature range 160–195 °C. Therefore, the larger domain sizes produced by annealing at 195 °C and a reduced interfacial thickness, which is predicted³⁴ to be inversely proportional to the square root of χ , imply that less material will be in the interfaces.

Figure 6 shows the values of T_{\max} of the first (if present) and second peak of the blends as a function of $\log t_a$ together with the pure component data presented before in Figure 3. Also shown are T_{ons} of the shoulder containing peaks and T_{ons} of pure PVC. A number of features are clearly visible: the T_{\max} of PiPMA and the second peak of the PVC/PiPMA blends coincide, the T_{\max} of PVC and the first peak of the PVC/PiPMA blends, where present, coincide, and finally the T_{ons} of PVC and the shoulder-containing peak of PVC/PiPMA blends coincide. From this we conclude that phase separation in PVC/PiPMA blends has taken place and that the composition of the two phases in equilibrium with each other is nearly pure PVC and PiPMA.

Blends of PVC and PMMA were investigated to compare these results with a related but miscible system. This system has the advantage of containing polymers with a

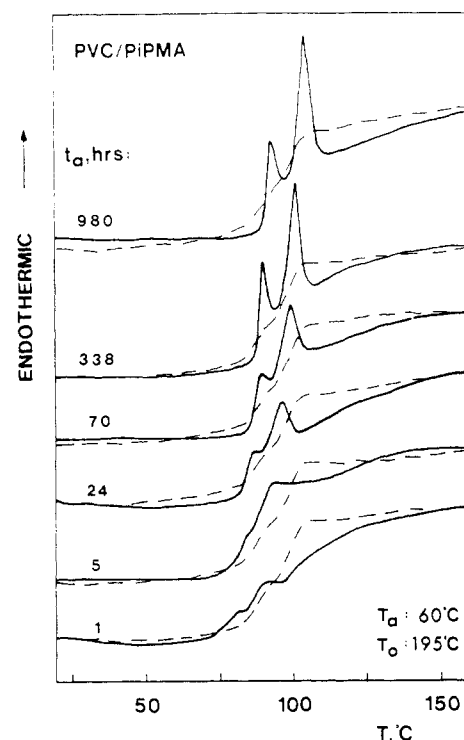


Figure 5. Thermograms of PVC/PiPMA, quenched from 195 °C and aged at 60 °C for the indicated times: first scan (—); second scan (---).

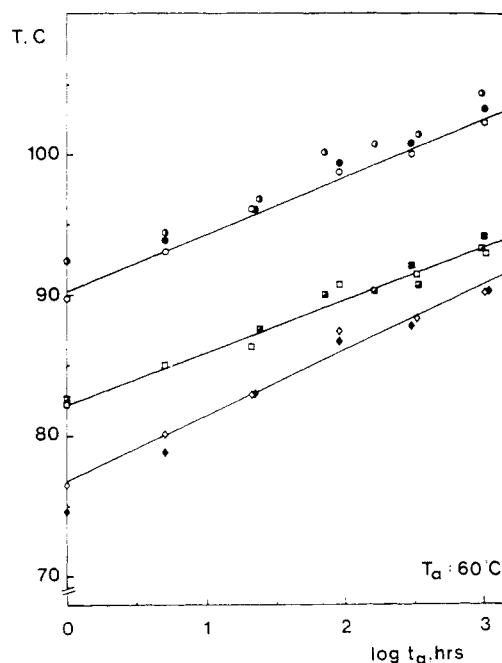


Figure 6. T_{\max} and T_{ons} versus $\log t_a$ for PiPMA, PVC, and PVC/PiPMA: (○) T_{\max} of PiPMA; (□) T_{\max} of PVC; (●, ■) T_{\max} of PVC/PiPMA ($T_0 = 160$ °C); (○, □) T_{\max} of PVC/PiPMA ($T_0 = 195$ °C); (◇) T_{ons} of PVC; (◆) T_{ons} of PVC/PiPMA ($T_0 = 160$ °C).

sufficiently different value of their respective glass transition temperatures. The single intermediate T_g criterion can therefore be used. The miscibility of PVC and PMMA depends strongly on the tacticity of PMMA.^{20,35} For isotactic PMMA of a molecular weight $M_w = 5000$, phase separation occurs already at temperatures exceeding 180 °C, whereas for atactic or syndiotactic PMMA this occurs only for molecular weights above $M_w = 100\,000$. The polymers used in this study are therefore miscible at 160 °C. Figures 7 and 8 show the thermograms of PVC/

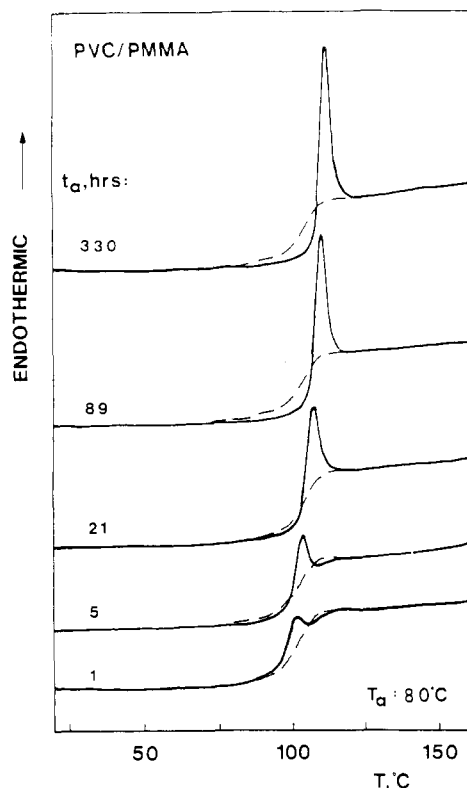


Figure 7. Thermograms of PVC/PMMA quenched from 160 °C and aged at 80 °C for the indicated times: first scan (—); second scan (---).

PMMA blends exposed at 160 °C for 5 min and aged at $T_a = 80, 60$, and 40 °C for the amounts of time indicated. Clearly, one single enthalpy recovery peak is present in all scans of the aged samples. Also one single intermediate T_g is visible in all the scans of the blends with erased physical aging history. The enthalpy recovery peaks observed have all the characteristics of a single pure component. The peak increases in magnitude and temperature with increasing aging time t_a and aging temperature T_a . This is demonstrated quantitatively in Figure 9, showing T_{max} as a function of $\log t_a$ for the three different aging temperatures.

Concluding Remarks

It is apparent that aging studies are an additional useful technique to study polymer-polymer miscibility. This has been demonstrated for an exacting polymer blend system where the T_g values of the two polymers were virtually coincident. The aging time does not necessarily have to be very large, and in the examples examined here a period of several hours was sufficiently long enough. At first sight, there seems to be two limitations to the present approach. For most systems the difference in aging behavior will not be as pronounced as for the model system considered here. However, in that case, a plot of the onset and the maximum of the enthalpy recovery peak as a function of $\log t_a$ becomes especially useful. If phase separation has occurred, the T_{ons} of the blend will resemble closely the T_{ons} of the pure component with the enthalpy recovery peak at the lowest temperature. The T_{max} of the blend, on the other hand, will resemble the T_{max} of the pure component with the enthalpy recovery peak at the highest temperatures. This situation actually occurred for the PVC/PiPMA blends annealed at 160 °C and aged at 60 °C for a short period, as demonstrated in the last section. The only real limitation seems to be the fact that the composition of the two phases in equilibrium should be sufficiently

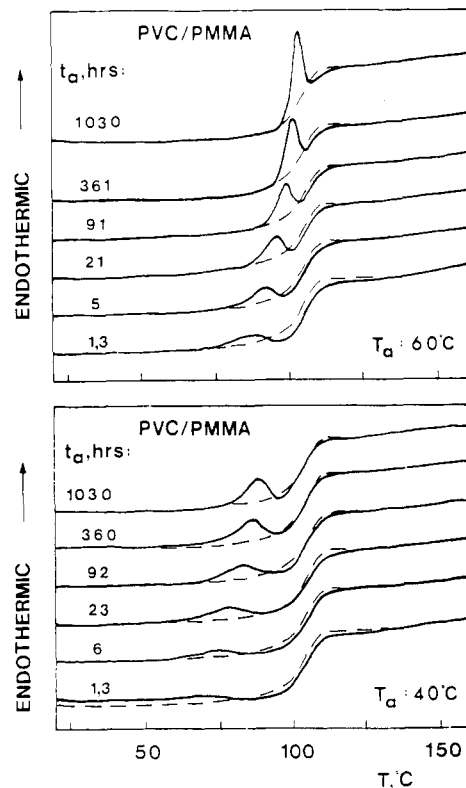


Figure 8. Thermograms of PVC/PMMA quenched from 160 °C and aged at 60 and 40 °C for the indicated times: first scan (—); second scan (---).

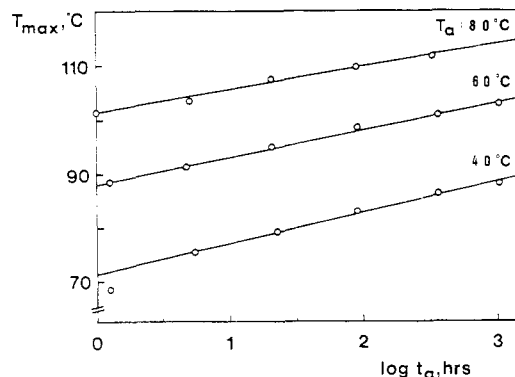


Figure 9. T_{max} versus $\log t_a$ for PVC/PMMA.

different. Except near the minimum of the cloud point curve, this will not pose any serious problem for polymer blends.

Although PVC/PiPMA can be considered a model system, in many respects it is not, as PVC can be a difficult material to characterize by calorimetry. Thus a quenched thermogram does not necessarily superimpose easily onto an aged thermogram. This can be seen by examining the thermograms shown in Figure 1. Accordingly, it becomes difficult to measure the enthalpy difference between the aged and unaged samples. This parameter can also be a useful quantity when attempting to establish polymer-polymer phase behavior. However, the complete immiscibility of PVC and PiPMA was readily apparent from measurements of T_{max} and T_{ons} , and it was unnecessary to make any measurements of the enthalpy difference.

Registry No. PVC, 9002-86-2; PiPMA, 26655-94-7; PMMA, 9011-14-7.

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Antiplasticization and Volumetric Behavior in Glassy Polymers

J. S. Vrentas,* J. L. Duda, and H.-C. Ling

Department of Chemical Engineering, The Pennsylvania State University, University Park, Pennsylvania 16802. Received August 25, 1987

ABSTRACT: A model is proposed for understanding changes in the volumetric and the free-volume properties of a glassy polymer upon addition of a low molecular weight diluent. The proposed theory for volumetric behavior appears to describe the negative departures from volume additivity that have been observed experimentally in glassy polymer-diluent systems. An expression is derived for the concentration dependence of the specific hole free volume in a glassy polymer-diluent mixture. This expression is used to explain antiplasticization behavior in glassy polymers and to rank the antiplasticization effectiveness of various diluents that are added to a particular polymer glass.

Introduction

When certain low molecular weight materials are added to glassy polymers, motions in the polymer chain appear to be retarded, and the mechanical behavior of the material is the opposite of that observed when plasticizers are added to a polymer. This type of behavior has been termed antiplasticization, and it is thought that this phenomenon is somehow related to a loss in free volume and a subsequent suppression of motions in the polymer chain.¹⁻⁴ Volumetric data for polymer-diluent mixtures have shown a significant negative departure from volume additivity,^{2,3} and it seems reasonable to suppose that this leads to a loss in the free volume of the system. Although this general picture appears plausible, there has been no comprehensive attempt to provide a quantitative description of the volumetric and free-volume behavior of glassy polymer-diluent systems. The objective of this article is thus to propose a model for understanding changes in the volumetric and the free-volume properties of a glassy polymer upon addition of a low molecular weight diluent.

Since glassy polymer properties are history dependent, this model is necessarily restricted, in the strictest sense, to polymer-diluent samples that are prepared in a prescribed manner. However, the sample preparation history that will be utilized is a reasonable one, and, furthermore, the formulation of a quantitative model leads to a better

general understanding of antiplasticization and of volumetric behavior in glassy polymers even when different sample preparation histories are used. The assumptions used in the model are listed in the second section of the paper, and predictions of the theory are developed in the third section. A comparison of the theory with experimental data is presented in the final section.

Assumptions of the Model

The following assumptions are used in the development of a theory describing the volumetric behavior of polymer-diluent systems in the glassy state:

(1) Transport behavior in the glassy polymer-diluent mixture is governed by the amount of specific hole free volume in the polymeric system.

(2) For most of the calculations carried out in this article, the various volumes required for the theory are calculated by using thermal expansion coefficients that are approximated by average values in the temperature range under consideration. Furthermore, for all expansion coefficients utilized in the theory and for the temperature intervals of interest, it is assumed that approximations of the type

$$\exp[\alpha_2(T - T_{g2})] = 1 + \alpha_2(T - T_{g2}) \quad (1)$$

are sufficiently accurate. In this equation, α_2 is the thermal expansion coefficient for the equilibrium liquid polymer,