The thermal characterization of multi-component systems by enthalpy relaxation

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Abstract

The phenomenon of enthalpy relaxation of amorphous glassy polymers has been developed into an analytical tool which can be applied to elucidate phase behavior and morphologically related phenomena of multi-component systems. We have both reviewed the experimental details concerning its application, using differential scanning calorimetry (DSC), and analyzed the theoretical basis for the effectiveness of the technique within the framework of the description by Moynihan and co-workers of relaxation in glassy systems. A summary of the adaption of this model, together with some new relevant examples, to mimic the experimental response of a multi-phase system is also presented. Although the technique was developed initially to examine phase phenomena in mixtures where behavior was difficult to resolve, owing to a close proximity of respective glass transition temperatures, we also document its evolution in addressing different situations including interfacial phenomena in semi-crystalline/amorphous polymer mixtures and block copolymers. Future directions for application of the technique are also briefly considered.

INTRODUCTION

The most simple and frequently applied feature for assessing phase phenomena in polymer mixtures and multi-component systems is the glass transition temperature T_g. An accepted unambiguous criterion for the occurrence of miscibility, the presence of a molecularly homogeneous phase, is a single T_g which is typically close to that projected by conventional additivity rules [1–3]. The detection of multiple transitions, coincident with or shifted from those of the pure components, provides information on phase-separated or partially miscible systems. Although

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debate has at times focused on the critical domain size necessary for the manifestation of a unique T_g, the preceding conditions apply to the majority of multi-component systems. This includes mixtures containing a miscible crystallizable component; however, complications in identifying the nature of a mixed amorphous phase can result owing to morphological developments.

In view of the foregoing, it follows that thermoanalytical procedures, such as differential scanning calorimetry (DSC) and dynamical mechanical analysis (DMA), constitute the primary methods of analysis. DSC is chosen most often because of its superior efficiency, a scanning rate of 10–20°C min^{-1} compared to 1–2°C min^{-1} for a typical DMA experiment. An additional advantage is the uncomplicated sample preparation involving relatively small quantities of material, ≈ 10 mg. DSC also allows measurement of the incremental change in heat capacity ΔC_p, at T_g which can also be used to provide quantitative information with regard to mass balance in multi-component systems [4–6]. DMA has a special advantage over DSC based upon its ability to reveal secondary relaxations and transitional behavior resulting from small quantities (<10%) of a particular phase.

Aside from these individual concerns, it has always been believed that an important prerequisite for the implementation of these procedures is that the T_g of the various components should be sufficiently far apart, so that the resolution of transitional behavior of the multi-component material is possible. It has often been proposed that 10–20°C represents a minimum separation and that for components whose respective T_g values are less than 10°C apart, resolution of phase behavior may prove to be impossible. There are a substantial number of reports [7–16] referring to this restriction or involving circumstances such as that described above, where alternative, and sometimes less informative, procedures had to be adopted or in some instances comprehensive studies had to be curtailed. Some investigations [17–19] have illustrated the use of derivative thermograms for resolving phase behavior when the components of a polymer blend possessed T_g values of the order of 20°C apart. However, recent studies [20–27] have now shown that the limiting conditions described above are essentially superfluous and that resolution may be possible even when the constituents manifest an identical T_g. This has been achieved by examination of the enthalpy recovery behavior of the glassy state, after annealing below the respective T_g. The experimental procedure retains the attractive simplicity inherent in a DSC experiment and therefore suggests an extensive applicability to many different situations. It is the purpose of this communication to review these recent advances and, in particular, to explore the potential and application of these procedures for investigating additional and unique situations in multi-component systems.

ENTHALPY RELAXATION IN POLYMERS

If the temperature of a glass-forming substance, such as an amorphous polymer, is reduced, a remarkable increase in viscosity and response time to external perturbations is observed. The system becomes sluggish and is no longer capable of following the decreasing temperature. It falls out of equilibrium at the so-called glass transition temperature, which will depend on the cooling rate employed. The exact nature of the glass transition is not yet clear but an important aspect of its manifestation is the reduction in configurational entropy. Adams and Gibbs [28] observed that relaxations involve the cooperative rearrangement of increasingly larger regions. The barrier to relaxation grows and ultimately diverges leading to an infinite viscosity. In practice, the kinetically determined glass transition temperature manifests itself by a change in slope of the enthalpy H or volume V versus temperature T, as presented schematically in Fig. 1. The abrupt change in slope of $H(T)$ at $T = T_g$ is reminiscent of a second-order phase transition in the Ehrenfest sense. The glass transition is not a true phase transition, although the presence of a real second-order phase transition in the limit of infinitely slow cooling [29] cannot be excluded. At temperatures below T_g, the system is in a non-equilibrium state and, consequently, the enthalpy H or volume V will decrease slowly upon annealing (aging) until the "equilibrium" value is reached.
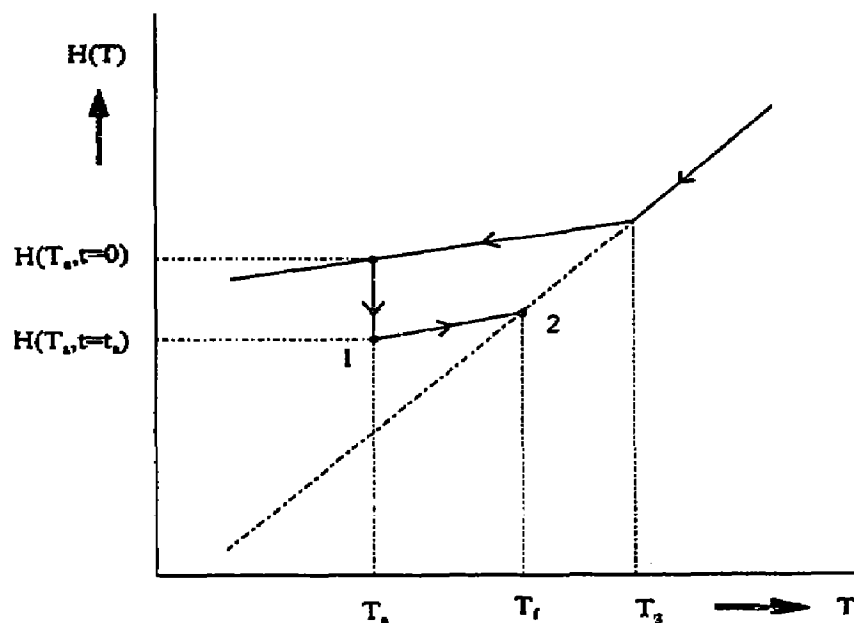

Fig. 1. Schematic representation of the path followed in a typical thermal analysis experiment demonstrating the memory effect. The characteristic parameters t_a, T_a, T_f and T_g are defined as shown.

Important information about the relaxation behavior in the glassy regime can be obtained from carefully designed experiments on previously aged samples. The experiments of Kovacs [30] are well known; he followed the volume of aged samples after a temperature jump to a higher temperature T_f, still below T_g, but chosen in such a way that the volume coincides with the value of the equilibrium volume at that temperature. Here we consider briefly the same experiment in terms of the enthalpy.

As indicated in Fig. 1, the aging at T_a produces a reduction in H from the original value $H(T_a, t = 0)$ to a value of $H(T_a, t = t_a)$ after annealing for a time t_a. At that time the structure of the system is characterized by the so-called fictive temperature T_f, defined as the temperature at which the system would apparently fall out of equilibrium for a cooling rate small enough to reach $H(T_a, t_a)$ at T_a during the cooling process. After this annealing procedure, the system is brought to T_f almost instantaneously at which, as indicated, the enthalpy obtained by the annealing happens to be the equilibrium enthalpy. However, at this stage the enthalpy does not behave as a constant function of time, rather it increases relatively fast, followed after a while by a slow decrease towards its initial value. This phenomenon is known as the memory effect: the system remembers its thermal history and at T_f most of the relaxation that occurred at T_a is recovered relatively fast and only after most of the recovery has taken place do the relaxation processes at T_f take over. This behavior is characteristic for the glassy state of matter and demonstrates an important principle first formulated by Struik [31]: "the aging which has occurred at some temperature T_a can be erased partially or completely by heating the material to a temperature that may be considerably below T_g".

If, instead of being brought almost instantaneously from the aging temperature T_a to the corresponding fictive temperature T_f, the system is heated through the glass transition with a finite rate, of the order of 10–20°C min^{-1}, this memory effect may still lead to an enthalpy recovery below T_g. In that case, the constant pressure heat capacity $C_p(T)$ (DSC) curve, i.e. the temperature derivative of the enthalpy, shows an enthalpy recovery peak prior to the ΔC_p, associated with T_g. However, the more common situation is an overshoot, with an enthalpy recovery peak superimposed on the specific heat jump at T_g. These different possibilities are illustrated in Fig. 2.

The currently favored theoretical description of the enthalpy relaxation in the non-equilibrium glassy state of polymers is the one introduced by Moynihan et al. [32]. Its application to polymer systems has been documented extensively by Hodge and Berens [33–35]. It is expressed in terms of the function

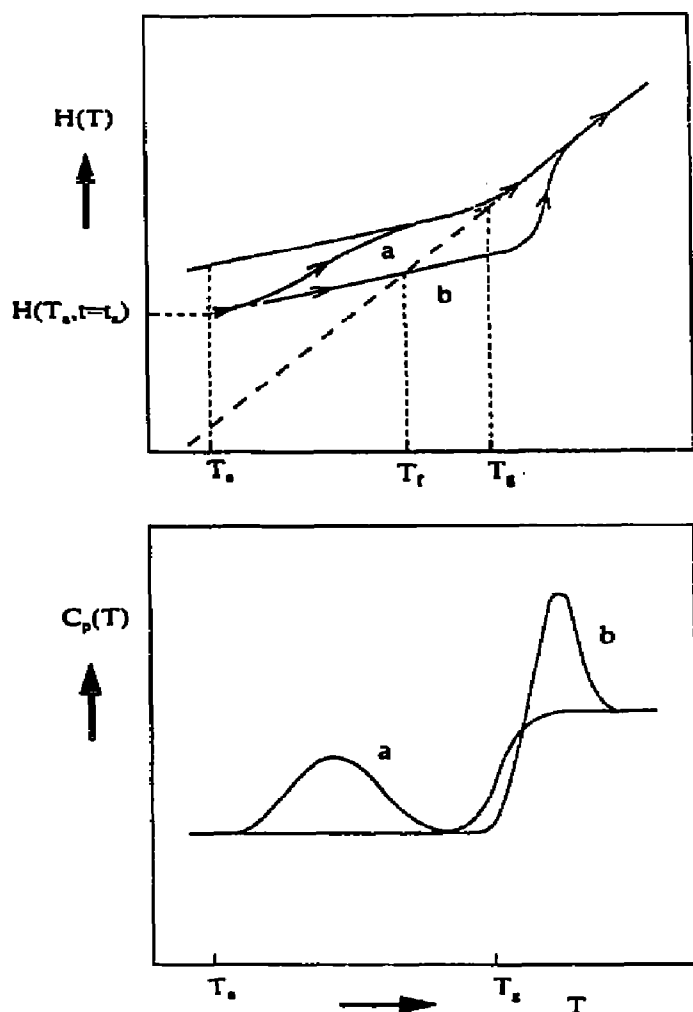$$\Phi(t) = \frac{H(T_a, t) - H(T_a, \infty)}{H(T_a, 0) - H(T_a, \infty)}$$

Fig. 2. Schematic representation of two possible kinds of curves of an aged sample obtained by DSC and the corresponding paths in the enthalpy–temperature plane. Endotherm direction upwards.

where $\Phi(t)$ is described according to the theoretical model given by the Kohlrausch Williams-Watts form

$$\Phi(t) = \exp(-(t/\tau)^{\beta}) \tag{2}$$

The relaxation time τ is given by

$$\tau = A \exp\left[\frac{x\Delta h}{RT_a} + \frac{(1-x)\Delta h}{RT_f}\right] \tag{3}$$

In these equations, β is the non-exponentiality parameter $(0 < \beta < 1)$, x the non-linearity parameter, Δh an activation enthalpy and A a pre-exponential factor. The parameter x partitions the exponent of the relaxation time between a purely Arrhenius-type behavior and a purely structurally

determined behavior. A value of x smaller than unity makes part of the relaxation structural-dependent, which implies that the relaxation towards equilibrium at a temperature T_n below T_g will depend on whether this temperature was reached from a temperature jump from a lower or a higher temperature. A value of β smaller than unity corresponds to a distribution of relaxation times and is absolutely essential for a description of the memory effect discussed before. This particular form of the phenomeno-logical description of relaxation phenomena in the glassy state is due to Moynihan et al. [32] who introduced the non-linearity parameter into the original Gardon and Narayanaswamy [36] expression. An alternative but similar theoretical description has been put forward by Kovacs et al. [37].

Using Botzmann's superposition principle, eqns. (1)–(3) can be used to describe the enthalpic response of a glassy material to time-dependent heating or cooling procedures as applied in common DSC experiments. Cooling or heating is modelled by discrete temperature jumps that correspond to the rate of change employed. The response is expressed in terms of the fictive temperature T_f whose value after n temperature steps is given by

$$T_f(n) = T_0 + \sum_{j=1}^{n} \Delta T(j)\left(1 - \exp\left[-\left(\sum_{k=j}^{n} \Delta T(k)/Q(k)\tau_0(k)\right)^{\beta}\right]\right) \qquad (4)$$

where T_0 is a starting temperature above the glass transition temperature, $Q(k)$ the cooling rate, $\Delta T(j)$ the temperature jump at the jth step, and $\tau_0(k)$ the relaxation time given by eqn. (3), with T_f given by the fictive temperature after $k - 1$ temperature jumps $T_f(k - 1)$, and T given by $T(k)$, the temperature reached after k temperature jumps. The normalized heat capacity is defined by

$$C_p^N(T) \equiv \frac{C_p(T) - C_{p,g}(T)}{C_{p,l}(T_f) - C_{p,g}(T_f)} \qquad (5)$$

where the subscripts g and l refer to the glassy and liquid state. The normalized heat capacity is directly related to the fictive temperature calculated according to eqn. (4) by the expression

$$C_p^N(T(n)) \approx \frac{\mathrm{d}T_f(n)}{\mathrm{d}T} \cong \frac{[T_f(n) - T_f(n - 1)]}{[T(n) - T(n - 1)]} \qquad (6)$$

During annealing, T is fixed and the ratio of $\Delta T(k)/Q(k)$ is replaced by a set of annealing times logarithmically evenly spaced in the annealing time interval $(0, t_a)$. The benefits of being able to model enthalpy recovery peaks in polymer using the formalism outlined will be illustrated in the following sections.

ENTHALPY RELAXATION OF POLYMER BLENDS

Background

Although enthalpy relaxation, or physical aging, of glassy materials has been a widely studied phenomenon [38], the inclusion of polymer mixtures has until recently been rather incidental [39] or somewhat brief. Early interest [40] in miscible blends of poly(methyl methacrylate)/poly(stryene-co-acrylonitrile), centered on the potential of molecular interactions to influence enthalpy recovery peaks produced by DSC. No effects were discernable, however: the miscible blends exhibited a single recovery peak. Further investigations [41] of miscible blends were also concerned with the potential of enthalpy relaxation to probe blend structure, specifically with regard to the transition broadening of polystyrene/poly(vinyl methyl ether) mixtures. A more recent in-depth analysis of the latter [42] concluded that aging processes were retarded in the blend and that the amount of relaxation occurring was smaller when compared to the pure components. However, studies [43] of miscible blends of polystyrene/poly(2,6-dimethyl-1,4-phenylene oxide) suggested that transition-width broadening, which can be attributed to concentration fluctuations, could also facilitate a similar result.

The foregoing discussion, together with studies reported by other workers [44,45], highlights the ability of enthalpy relaxation or physical aging to provide fundamental information concerning molecular processes and structure in multi-component systems. However, the principal focus of this communication is to review how the phenomenon can be applied to the characterization of multi-component systems and, as alluded to in our introductory comments, particularly those systems which are normally considered difficult to analyze by conventional thermal analysis. It has been noted on several occasions [20,3] that enthalpy recovery peaks are very informative when dealing with the phase behavior of systems which do not exhibit definitive transitional behavior. In the ensuing sections we will review how the phenomenon has been developed to constitute an important analytical procedure with a wide applicability to many different categories of polymer mixtures.

Enthalpy relaxation as an analytical tool

Enthalpy relaxation of a glassy material, and the recovery process on heating, is also accompanied by equivalent volumetric changes. In principle, both may be monitored for analytical purposes; however, specific heat rather than density is more accessible for measurements. Modern differential scanning calorimeters are very efficient and sensitive, and because enthalpy recovery is essentially a kinetic process, i.e. the
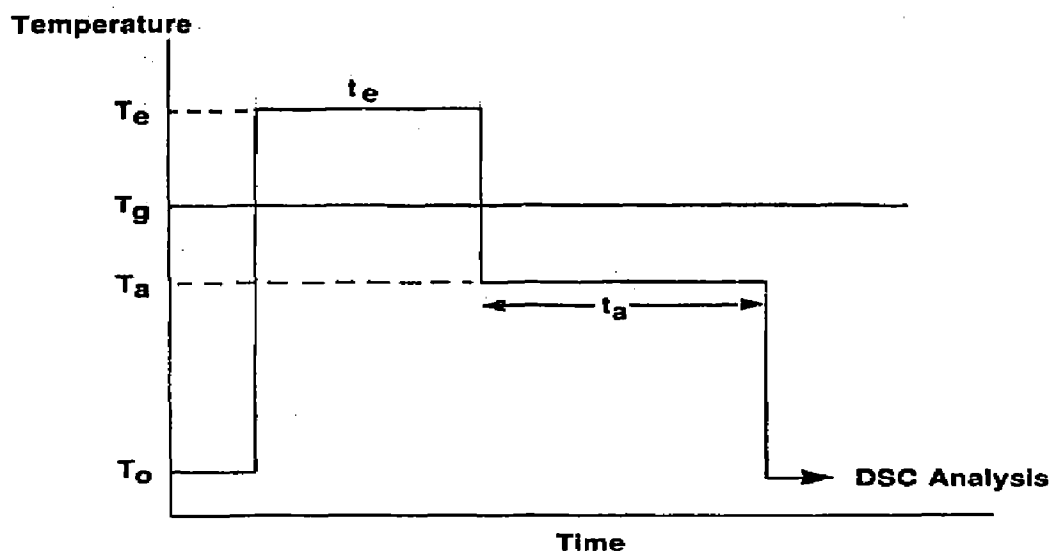
Fig. 3. Schematic representation of the time–temperature profile for conducting an enthalpy recovery experiment in a DSC.

magnitude of the recovery peak is dependent upon heating rate, relatively fast heating rates ($10\text{–}40°C\,min^{-1}$) can and, indeed, should be used; $20°C\,min^{-1}$ may be considered an optimum.

A typical temperature–time profile, which may be applied to a sample within the calorimeter sample chamber, is given schematically in Fig. 3. The equilibration temperature T_e should be at least 20°C above the T_g of the polymer. Under these conditions, only a short time (1–5 min) is needed to reach an equilibrium liquid state, after which the sample should be quenched to an ageing temperature T_a below T_g for a suitable aging time t_a. DSC analysis can be applied subsequently to provide thermograms as in Fig. 2. Modern computer-controlled calorimeters allow for a subtraction of one thermogram from the other to give heat changes arising solely from the enthalpy recovery, as indicated in Fig. 4. From these figures, the parameters T_{ons}, T_{max}, H_D and h_r may be determined. Some polymers exhibit small recovery peaks even when "quenched". This occurs due to the small amount of relaxation that can occur during the finite time that is spent just below T_g during both the cooling and heating cycles of the analysis itself.

For the evaluation of phase separation in polymer blends, the appearance of multiple recovery peaks is obviously symptomatic of heterogeneous blends. If mixing is homogeneous on a molecular level, then the co-operative nature of the relaxation processes implies that a single recovery peak will be observed whose position and magnitude now reflect the mixture and not the pure components. Often, this may be sufficient information for the purposes of determining phase behavior; however,
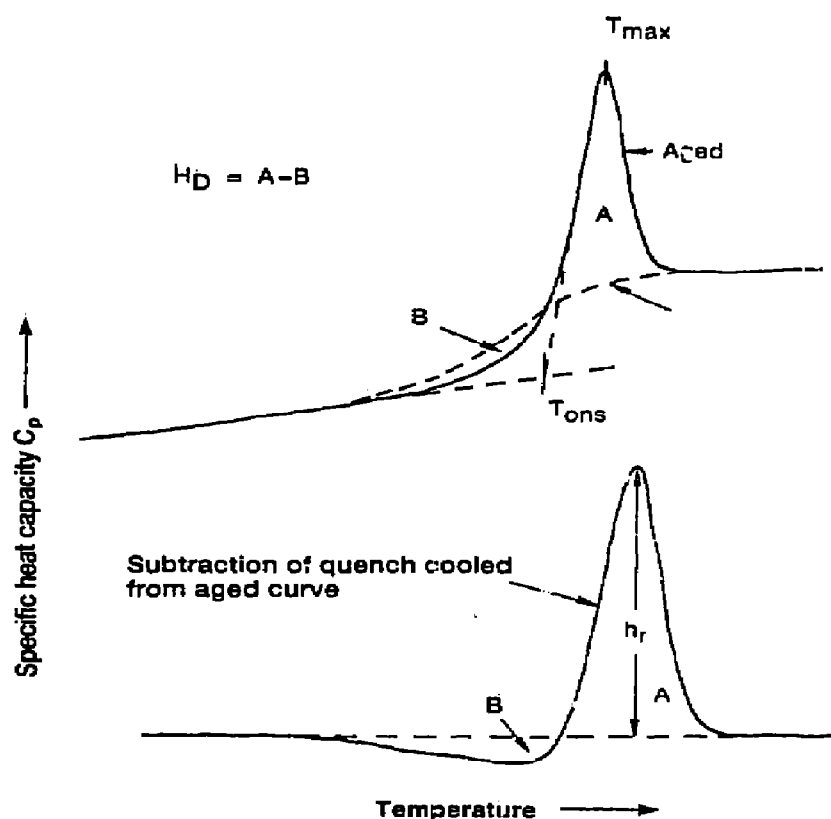
Fig. 4. Representative curves of an ..ged sample and a quench-cooled sample obtained by DSC. The parameters H_D, h_r, T_{ons} and T_{max} are defined as shown (reprinted with permission from ref. 26). Endotherm direction upwards.

careful scrutiny of the parameters noted above can be used to provide additional information. T_{max}, together with T_{ons} and H_D, will be linear when plotted as a function of $\log t_a$, provided that T_a is not too close to T_g. If this is the case, the parameters defining the recovery peak will stabilize and level off as thermodynamic equilibrium is attained. In a blend, this may hinder the ability to resolve behavior. If, however, T_a is too far below T_g, relaxation will be very slow and impractical. The optimum choice of $T_g - T_a$ has been discussed previously [24, 25]. A value of 15–20°C appears to be most appropriate. Of all physical parameters, only this one is within easy control of the experimentalist. An alternative and equally effective experimental approach has been proposed by other workers [46], whereby rather than maintaining T_a constant and characterizing the recovery peaks as a function of t_a, t_a is kept constant while T_a is varied. The most efficient strategy to adopt obviously depends upon the nature of the polymer mixture.

The quantities H_D and h_r can be used to provide additional information;

however, in studies where considerable transition-broadening occurs, as noted above, these quantities will be modified by composition fluctuations in the blend and will not reflect recovery of the blend as a whole aged at a fixed temperature below T_g. An additional experimental concern involves the recovery peaks in a phase-separated blend that are similar in magnitude and lie very close to each other. A rigorous evaluation of T_{max} would require deconvolution of the two recovery peaks which are superimposed upon each other. In most instances reported to date, this has been considered unnecessary.

Enthalpy relaxation of amorphous blends

Investigations of polymer blends have progressed from identifying isolated polymer pairs to include a determination of how chemical structure and composition influence phase behavior [47, 48]. Quite often, this will involve examining a large matrix of polymer pairs which differ little in chemical composition. Consequently, the T_g values of the components are very close to each other and it is in these situations that conventional thermal analysis may be found lacking. Several research groups, notably those of Cowie [49–53] and Goh [54–63], have reported a large number of studies which typify the circumstances described above and have implemented enthalpy recovery studies as an analytical tool. In general, most of these investigations have involved blends at 50:50 w/w composition and relied upon the appearance of single or multiple recovery peaks in order to assign phase behavior. In several instances [60, 62], blends whose respective T_g values were very close together (separated by as little as 2°C) could not be resolved; however, a more exhaustive analysis, applying procedures discussed below, appears not to have been attempted.

The references cited above, together with a wide variety of other blend studies [24, 25, 64–69] where enthalpy recovery characteristics have been used to ascertain phase behavior, are comprised exclusely of mixtures of completely amorphous polymers [70]. Evaluation of phase phenomena in binary blends of non-crystallizable polymers constitutes the most straight-forward analytical situation. In cases where immiscibility or partial miscibility ensures, the small but finite degree of mixing that occurs at the interface between phases must also be considered. This will be discussed in more detail below. In a one-phase mixture, the enthalpy recovery peak is symptomatic of a single T_g. Moreover, the kinetics of the recovery process, measured in terms of the T_{max} or T_{min}, are also indicative of a homogeneous system, but intermediate between that of the pure components in the mixture. Both these features are illustrated in Figs. 5 and 6 for blends of PVC and PMMA [23], and a blend composed of aromatic polyamides [64]. For a heterogeneous mixture, the recovery peaks will obviously reflect multiple phases. The ability to differentiate behavior as the T_g values of the
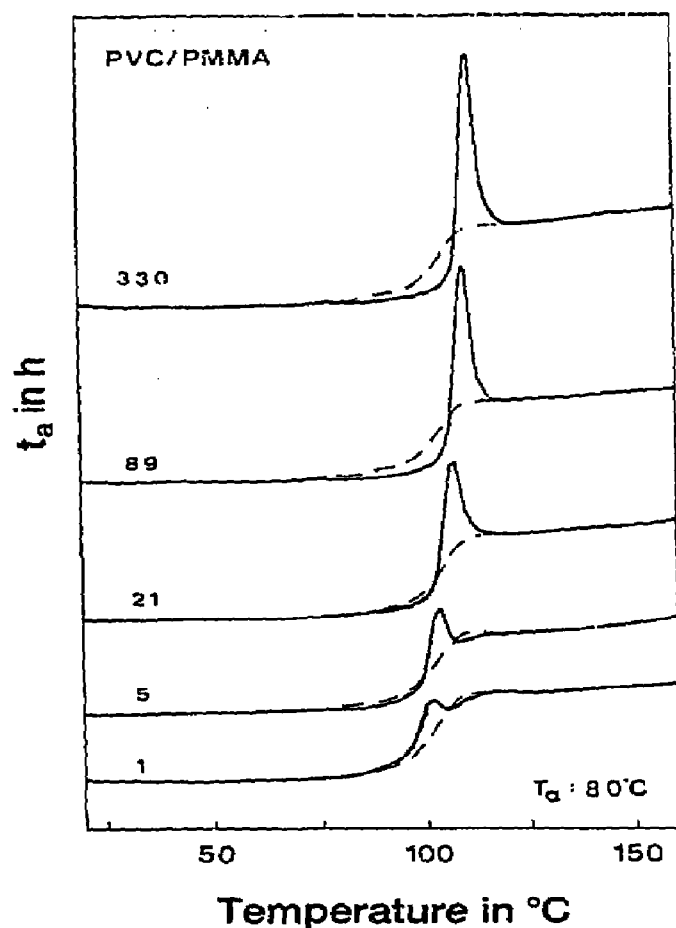
Fig. 5. Enthalpy recovery peaks obtained from miscible blends of PVC ($T_\mu = 80°C$) and PMMA ($T_\mu = 110°C$) (reprinted with permission from ref. 23). Endotherm direction upwards.

components move closer together will depend upon their effective aging times t_{eff} given by equation

$$t_{eff} = t_a / \tau \qquad (7)$$

The quantity τ (see eqn. (3)) is dependent upon the parameters x, Δh and A and the relaxation spectrum is related to β. Therefore, even if two polymers have a similar T_μ, a significant difference in the parameters noted above will result in significant differences in enthalpy relaxation at T_a and, therefore, in enthalpy recovery peaks. We can illustrate the foregoing by reference to blends of PVC ($T_\mu = 80.5°C$) and PiPMA ($T_\mu = 82.5°C$) as shown in Fig. 7. Here we compare experimentally observed recovery peaks with those generated by computer simulation, assuming phase separation into pure components with infinitely sharp phase boundaries. The parameters given for PiPMA and PVC are based on literature values for PMMA and PVC
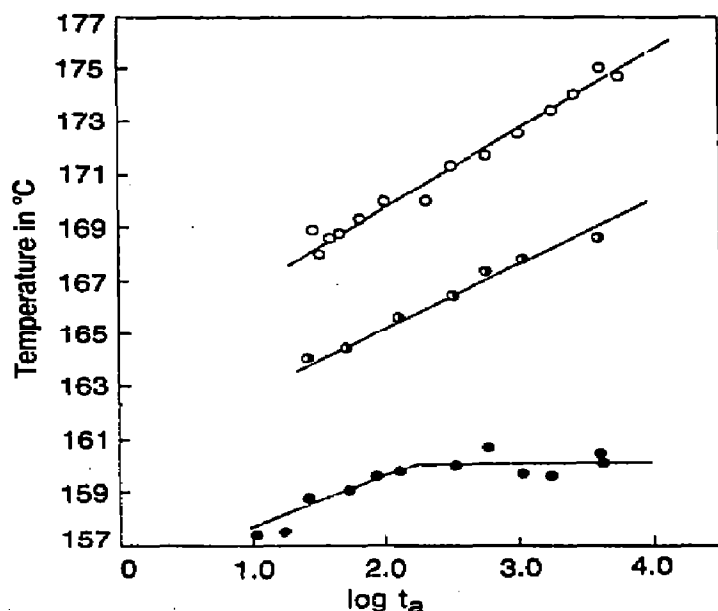
Fig. 6. Measurements of T_{max} for a miscible blend (◑) of two amorphous nylons (●, ○) with respective T_g values of 151 and 161°C ($T_g' = 143$°C). Note that T_{max} for the polymer with the lower T_g (●) stabilizes upon attaining thermodynamic equilibrium (reprinted with permission from ref. 26.)

respectively (Table 1). For both sets of data, $\Delta h/R$ was slightly reduced to correspond more closely to the T_g values mentioned. As can be seen the agreement between theory and experiment is satisfactory. Another point that should be noted is the occurrence of a pre-T_g peak coming from the recovery of the PVC component. PVC is well known for this feature [34] which is a clear manifestation of the memory effect alluded to above. Small values of β, corresponding to a broad spectrum of relaxation times, large values of $T_g - T_a$, and small values of t_a, favor this type of behavior. PVC and PiPMA behave quite differently with respect to enthalpy recovery, and separate enthalpy recovery peaks appear without much difficulty. This is no longer the case for polymers with a more similar relaxation behavior. Figure 8 shows the theoretically predicted behavior for a phase-separated blend of PS and PMMA simulated with parameter values taken from the literature (Table 1). In this specific case, much higher annealing times are required to resolve the enthalpy recovery peaks. For polymers of very similar relaxation behavior, and therefore similar parameters β, x, A and Δh, the separation of T_g values becomes more critical. For small values of t_a, T_f can be approximated by T_g and the relaxation time τ according to eqn. (3) is given by

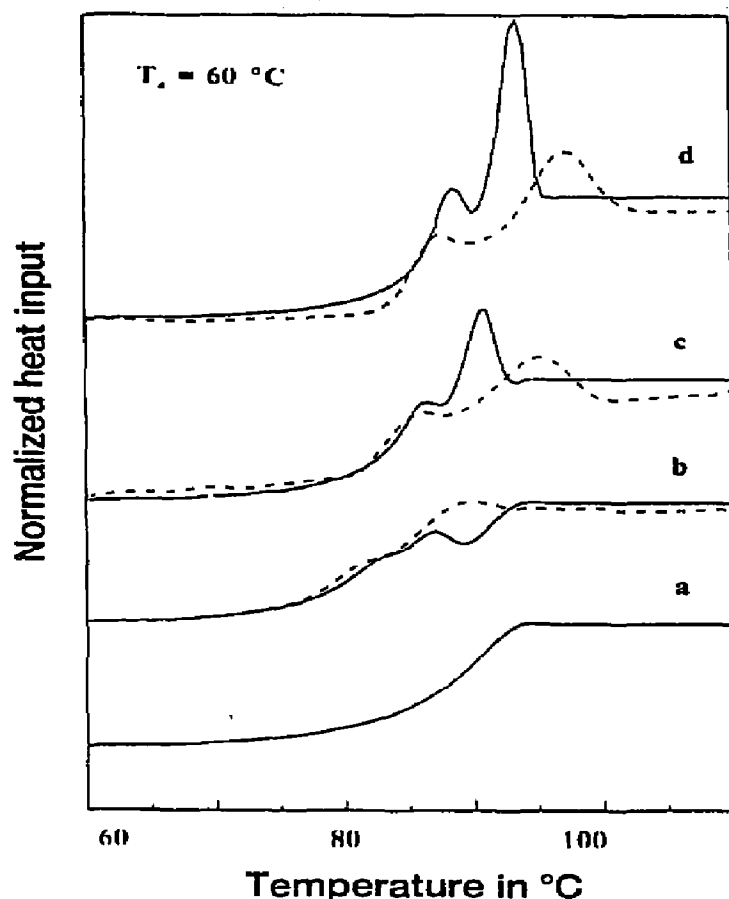$$\tau = \tau_0 \exp \frac{x\Delta h}{RT_a T_g} [T_g - T_a] \tag{8}$$

Fig. 7. Comparison between experimentally observed (– – –) and theoretically predicted
(—) enthalpy recovery peaks for a phase-separated blend of PVC ($T_g = 82°C$) and PiPMA
($T_g = 82.5°C$) for t_a: (a) 0 h; (b) 5 h; (c) 24 h; and (d) 70 h. Endotherm direction upwards.

TABLE 1

Parameter values

	β	x	$(\Delta h/R)/kK$	$\ln(A/s)$	$T_g/°C$ (onset)
PVC [a]	0.25	0.11	225	−619.0	80.5
PiPMA [b]	0.35	0.19	127	−357.8	82.5
PMMA [c]	0.35	0.19	138	−357.8	106.0
PS [d]	0.58	0.27	126	−328.8	104.0

[a] From ref. 34. [b] Data for PMMA from ref. 71 with $\Delta h/R$ slightly reduced. [c] From ref. 71.
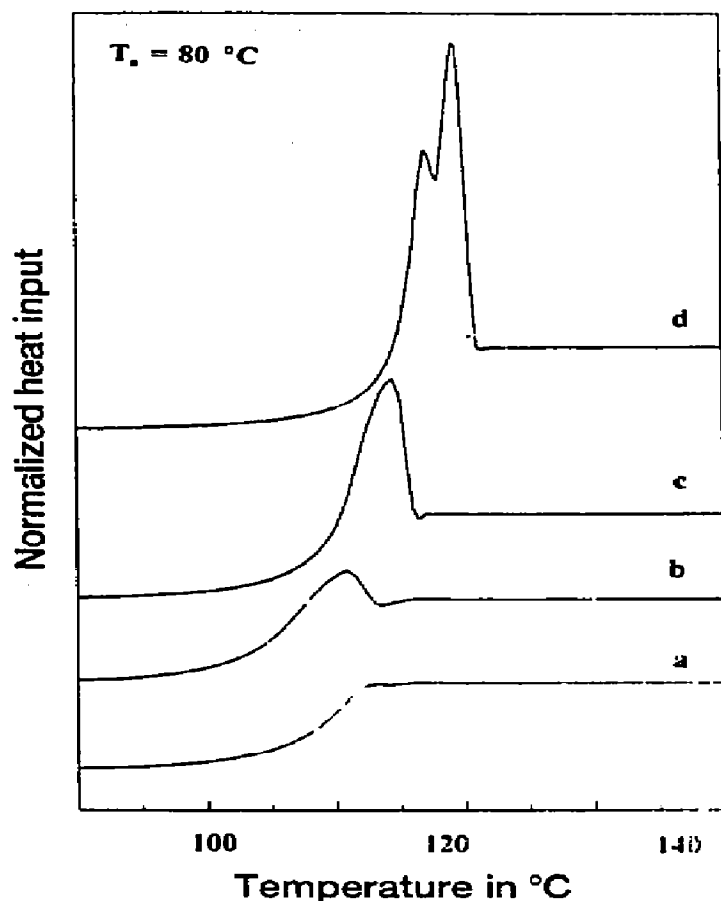[d] From ref. 43.

Fig. 8. Theoretically predicted enthalpy recovery peaks for a phase-separated blend of PS (T_{μ} = 104°C) and PMMA (T_{μ} = 106°C) for t_a: (a) 0 h; (b) 5 h; (c) 25 h; and (d) 125 h. Endotherm direction upwards.

Thus for two phases, the difference between their respective quantities $T_{\mu} - T_a$ will be a decisive factor in resolving their recovery peaks, and in effect needs to be maximized. In various studies dealing with PS and PMMA [20, 21, 46], the difference between the respective T_{μ} values is larger than the two degrees in the above-considered example and two separated peaks can readily be obtained.

The difficulty outlined above has been encountered experimentally [64] as an immiscible blend of aromatic polyamides whose structure and respective T_{μ} values (158 and 161°C) were extremely close together. Although multiple recovery peaks could not be observed, the position of T_{max} was identified with the higher T_{μ} phase, whereas T_{ons} was coincident with the lower T_{μ} phase (Fig. 9(a)). These observations are in themselves not conclusive of two-phase behavior; however, comparison of h_r, as shown in Fig. 9(b), provides compelling evidence against a conclusion of miscibility.
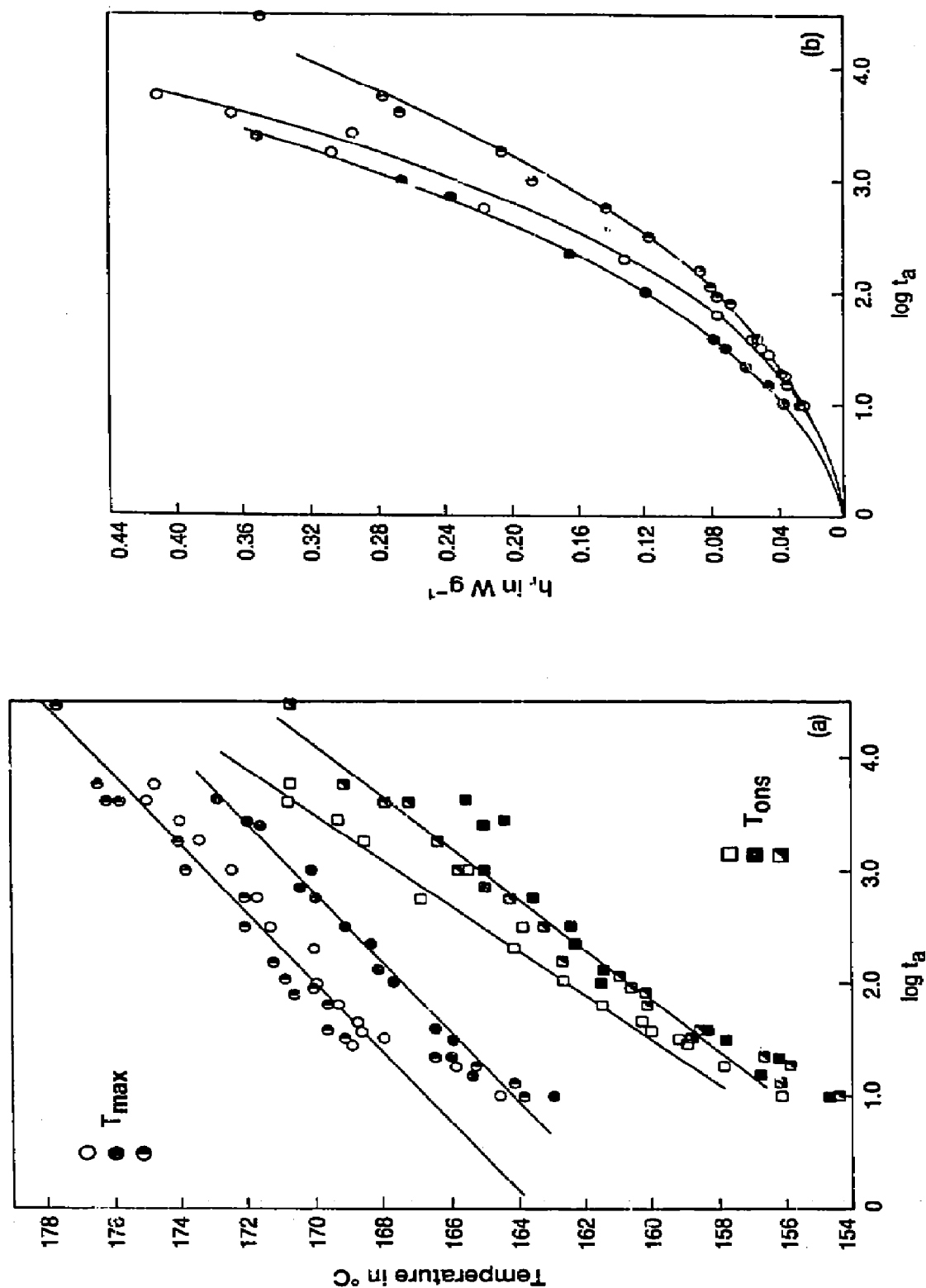
Fig. 9. (a) Measurement of T_{max} (O, ●, ◐) and T_{ons} (□, ■, ◪) for two amorphous nylons ($T_g = 161$ and $158°C$, respectively) and their blend ($T_g = 143°C$). Note that T_{max} of the single enthalpy recovery peak of the immiscible blend is coincident with the higher T_g component, whereas T_{ons} is coincident with the lower T_g polymer (reproduced with permission, ref. 26). (b) Measurements of h_r for the polymers and blend shown in (a). Note that the recovery peak height is almost half of that of either of the pure polymers, particularly at higher values of $\log t_a$ (reproduced with permission, ref. 26).

Enthalpy relaxation of crystalline blends

When one or both of the components of a polymer blend has the ability to crystallize, there are a number of situations that can serve to complicate the determination of phase behavior, which are related to the complex morphology that can result. If the components of the mixture can be melted to form an equilibrium liquid, and then vitrified by quench cooling without the occurrence of significant crystallization, then the analytical criteria and procedures are the same as those applied to amorphous systems. Figure 10 illustrates an example of the latter for blends based upon a copolyester–amide containing random copolyamides of caprolactam/laurolactam [72]. Both components of these blends are crystallizable; however, they crystallize slowly owing to their random configuration and can be vitrified quite easily. As may be inferred from the figure, two of the blends are miscible and the remaining four exhibit heterogeneous recovery behavior. There are additional reports in the literature [27, 73] in which enthalpy
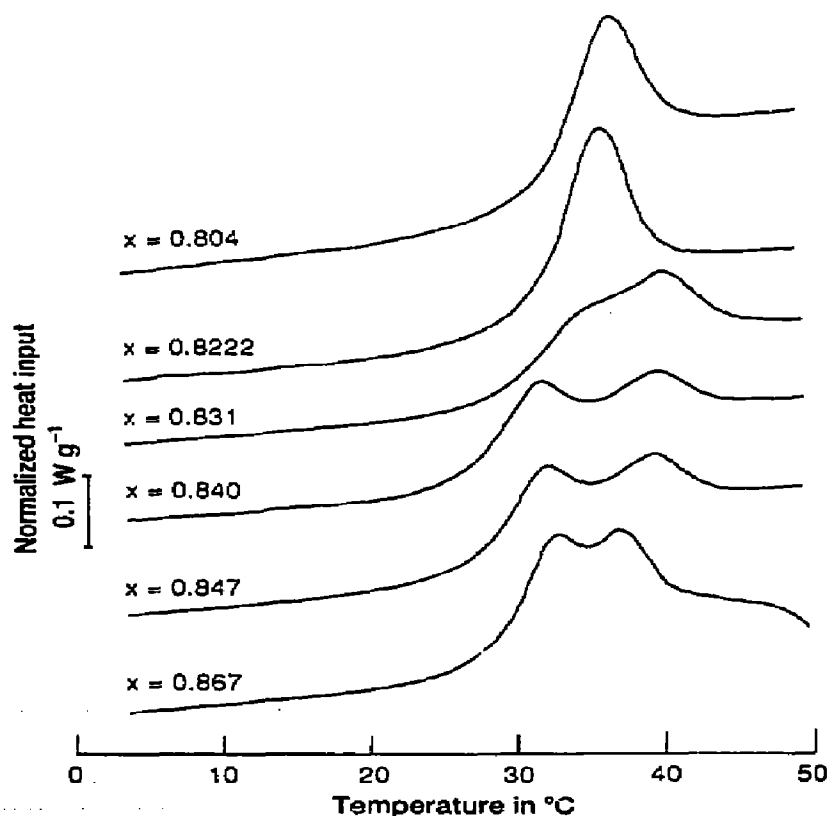
Fig. 10. Enthalpy recovery peaks obtained from blends of a copolyester–amide containing different aliphatic copolyamides of different composition (x is the volume fraction of methylene groups), $T_a = 15°C$, $t_a = 100$ min (reproduced with permission, ref. 84). Endotherm direction upwards.

recovery has been used to characterize phase behavior of crystalline/amorphous polymer blends.

When one or both of the polymers in the blend crystallizes so rapidly that the blend cannot be vitrified, the anaytical consequences can be more problematic. Crystallization of miscible amorphous/crystalline polymer blends can lead to heterogeneous quasi-two-phase amorphous regions which are capable of exhibiting heterogeneous relaxation behavior [74–84]. Locally, the morphology of the crystallized blend consists of a lamellar structure. If the interaction between both components is sufficiently favorable, the amorphous regions consist of order–disorder interphases of the pure semi-crystalline component and a mixed amorphous region [84]. The amount of material in the order–disorder interphases is small and sometimes difficult to detect. In this and similar cases, enthalpy relaxation may be used to enhance the detecting capabilities of thermal analysis and this will be discussed in the next section.

If the T_g values of both components are sufficiently far apart, the determination of the phase behavior does not present any difficulty provided that the presence of a mixed amorphous phase is taken as the decisive criterion for miscibility in the melt. However, when the T_g values are close together this is not the case. Blends of semi-crystalline aliphatic polyamides, e.g. nylon 4.6, nylon 6.6, etc., are excellent examples of the latter which have been examined using enthalpy recovery procedures. These materials have been found to display enthalpy recovery peaks, similar in nature to those of amorphous polymers; however, their magnitude is diminished considerably [85]. Crystallized blends of nylon 6.6 ($T_g = 52°C$) and nylon 6.12 ($T_g = 35°C$) did not exhibit multiple recovery peaks even though their respective T_g values are not particularly close. Quantitative analysis of T_{max} and T_{ons} as shown in Fig. 11 was interpreted as an indicator of phase separation; T_{max} was coincident with that of nylon 6.6 whereas T_{ons} was identified with nylon 6.12. An accompanying reduction in h_r was also noted for the blend. Blends of nylon 4.6 ($T_g = 59°C$) and nylon 6 ($T_g = 48°C$) were found to behave similarly; however, in this instance heterogeneous recovery behavior was observable at very long annealing times (5–6 days). This is illustrated in Fig. 12, which also contains a thermogram of the blend exhibiting a homogeneous recovery peak after exposure to high temperature. This has been interpreted as resulting from trans-reaction in the blend promoting a homogeneous amorphous phase.

Enthalpy relaxation of interfaces

So far we have looked at enthalpy relaxation as a method to identify different phases in situations where the conventional DSC analysis breaks down. The great success of this new method is due to the fact that the position of the enthalpy recovery peak is determined by the relaxation
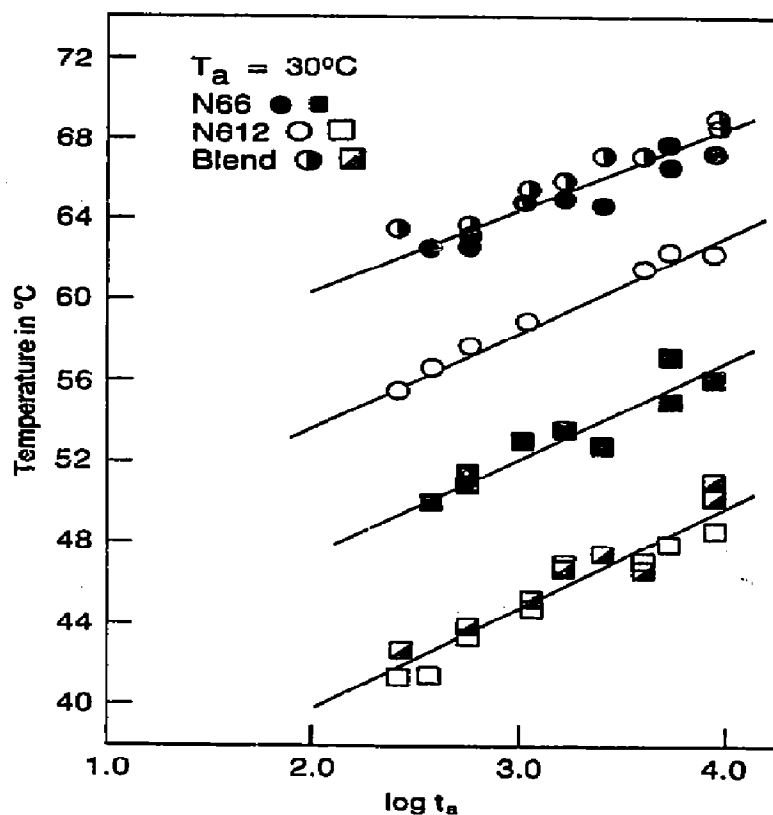
Fig. 11. Measurements of T_{max} (O, ●, ◑) and T_{ons} (□, ■, ◪) of crystalline polymers nylon 6.6, nylon 6.12 and their blends (T_a = 30°C). Note that T_{max} of the blend is coincident with that of nylon 6.6 whereas T_{ons} is coincident with that of nylon 6.12 (reproduced with permission, ref. 84).

behavior as a whole. The glass transition itself can be identified as the temperature for which the relaxation time τ is of the order of 1 min; this requirement alone is clearly deficient in fixing the complete relaxation spectrum. There is, however, another important feature; in a conventional DSC scan, the T_g manifests itself as a second-order phase transition whereas a similar scan from an aged sample shows the characteristics of a first-order transition. This fact is useful for the subject of polymer interfaces in polymer mixtures, because the amount of interfacial material may be estimated on the basis of enthalpy relaxation experiments. Two obvious candidates that contain an abundance of interfacial material are semi-crystalline polymer blends and mesomorphic block copolymer systems.

Semi-crystalline polymer blends

Blends of semi-crystalline PVDF and amorphous atactic PMMA may be regarded as a model system. The components are miscible in the melt and a spherulitic morphology is obtained after crystallization of PVDF. Locally, the system consists of a lamellar structure with alternating lamellae of
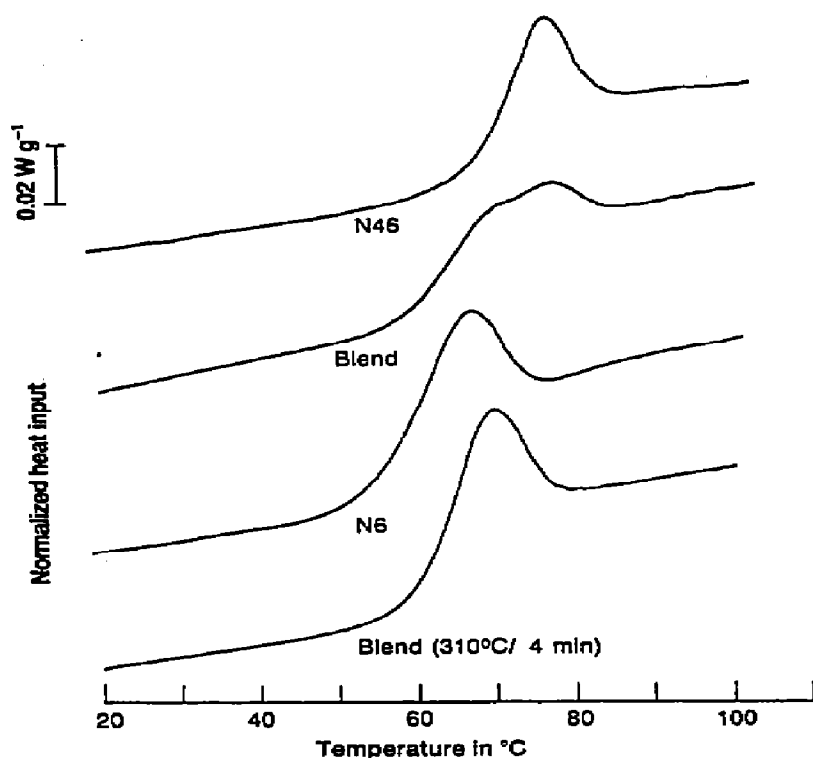
Fig. 12. Recovery peaks of crystalline polymers nylon 4.6, nylon 6 and their blend at values of $\log t_a \approx 3.9$ ($T_a = 40°C$). Note the change from a multiple recovery peak (B) in the blend to a single peak (D) after trans-reaction at 310°C for 4 min (reproduced with permission, ref. 84). Endotherm direction upwards.

crystalline PVDF, amorphous PVDF, i.e. the interface under consideration, and the amorphous mixed phase. The T_g values are far enough apart, $-40°C$ and $115°C$ for pure PVDF and PMMA respectively, to identify the two different amorphous phases in a conventional DSC scan. The signal due to the interface, however, is such that an estimate of the amount of interfacial material on the basis of the ΔC_p jump is almost impossible. A reasonable estimate can be obtained from an appropriate enthalpy relaxation experiment. To see this we note that the maximum amount of enthalpy relaxation at a given ageing temperature T_a has occurred once equilibrium is reached. Referring to Fig. 1, this amount, ΔH_∞, is related to the heat capacity jump $\Delta C_p = C_{p,l} - C_{p,g}$ by

$$\Delta H_\infty = H(T_a, t_a = 0) - H(T_a, t_a = \infty) = \Delta C_p(T_g - T_a) \qquad (9)$$

A measurement of ΔH_∞, therefore, determines the amount of material involved provided the other physical parameters are known, which is usually the case. An example for the system PVDF/PMMA (75/25 w/w %)
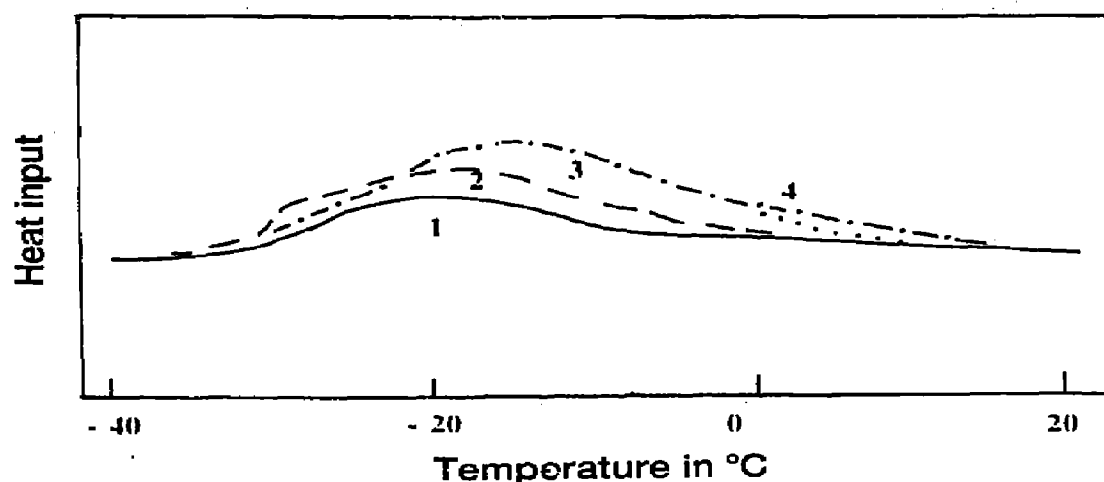
Fig. 13. Enthalpy relaxation peaks for PVDF/PMMA blends (25/75 w/w %), isothermally crystallized at 50°C and aged at $T_a = -50°C$ for $t_a = 2$ h (1), 5 h (2), 17 h (3) and 24 h (4). Endotherm direction upwards.

is given in Fig. 13. From these results, it was inferred that almost complete relaxation had occurred for $t_a > 20$ h, and from eqn. (9) the amount of interfacial PVDF was estimated to be 32% w/w of all PVDF in the sample [83].

Block copolymer systems

The application of enthalpy relaxation as an analytic tool to determine the amount of interfacial material in block copolymer systems was initiated by Quan et al. [86]. They consider micro-phase-separated systems of styrene–isoprene–styrene tri-block copolymers. As in the case of PMMA/PVDF, the tri-block copolymer system contains domains of completely different T_g values ($-50°C$ and $100°C$ for isoprene and styrene, respectively). The analysis to determine the amount of interfacial material is based on the premise that in the interface between the styrene and isoprene phase, the T_g varies linearly through the interface between the two extremes of the pure components. Aging at a temperature between the two T_g values of the pure components gives rise to relaxation of a part of the interface, provided only that the aging temperature is sufficiently far below the T_g of the styrene phase preventing noticeable relaxation of the latter. If the total amount of interfacial material is denoted by F, the amount of interfacial material with a glass transition temperature in between T_g and $T_g + dT_g$, dF, is given by

$$dF = \frac{F}{T_{g,s} - T_{g,i}} dT_g = \frac{F}{\Delta T_g} dT_g \qquad (10)$$

where $T_{g,i}$ and $T_{g,s}$ represent the T_g of polyisoprene and polystyrene,
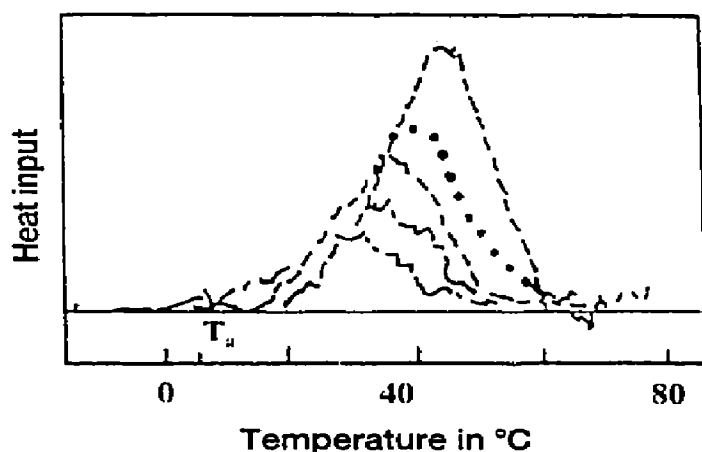
Fig. 14. Difference between annelaed and quenched runs of styrene–isoprene–styrene block copolymers containing in addition 10% w/w of polyisoprene. The respective runs correspond to different annealing times, $T_{\rm a} = 5°{\rm C}$ [86]. Endotherm direction upwards.

respectively. Aging at an appropriate temperature $T_{\rm a}$ gives rise to an enthalpy recovery peak due to the interface, as illustrated in Fig. 14 [86]. From data of this type, the amount of interfacial material may be derived provided an assumption is made concerning which part of the interface has undergone complete relaxation. The authors of ref. 86 assumed that the part of the interface with a glass transition temperature satisfying $T_{\rm a} \leq T_{\rm g} \leq T_{\rm max}$ is fully relaxed, where $T_{\rm max}$ is the temperature of the position of the maximum of the enthalpy relaxation peak, which obviously depends on $T_{\rm a}$ as well as $t_{\rm a}$. Furthermore, they assumed that the part of the enthalpy relaxation peak below $T_{\rm max}$, $\Delta H_{\rm e}$, corresponds to the enthalpy relaxation of this fully relaxed part of the interface. These assumptions, together with eqns. (9) and (10), imply that

$$\Delta H_{\rm e} = \int_{T_{\rm a}}^{T_{\rm max}} \Delta H_x(T_{\rm g})\, {\rm d}F = \frac{F\Delta C_p}{2\Delta T_{\rm g}} (T_{\rm max} - T_{\rm a})^2 \tag{11}$$

It is this expression that was used by Quan et al. to calculate F for various tri-block copolymer systems. Subsequent to this work, several other research groups [46, 87, 88] have recognized the potential of enthalpy relaxation to characterize the behavior of block copolymers.

CONCLUDING REMARKS

We have illustrated the implementation of enthalpy recovery to decipher phase phenomena of ambiguous multi-component polymer systems in several different situations. This type of analysis need not be restricted to circumstances in which the respective $T_{\rm g}$ values of the components are close to each other because it can also provide decisive information whenever

there is doubt concerning subtle or uncertain thermal behavior. Light scattering and other techniques that probe phase behavior remain very useful; however, we believe that enthalpy recovery measurements have the potential to provide unique information for certain kinds of mixtures.

If for a moment we consider future applications, we note that most investigations to date have involved mixtures in equilibrium. Phase separation processes, such as spinodal decomposition and nucleation and growth, or segregation processes in crystallizable polymer mixtures, proceed by different mechanisms and lead to distributions of species. In certain instances, enthalpy recovery measurements may be used to probe these dynamic phenomena and provide information as a function of time. If such an analysis is possible, then the ability to model the recovery process, such as the Moynihan approach discussed here, will be a vital ingredient.

This modelling is also essential for a judgement of the assumption made so far in the determination of the amount of interfacial material in micro-phase-separated block copolymer systems and may lead to other more accurate assumptions [89]. It may even turn out that different systems require different assumptions. In this respect, the physical significance of the parameters contained in the mathematical description becomes of interest. Suggestions about their relation with molecular properties have been given [90], but it remains rather obscure.

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