

A novel use of physical aging to distinguish immiscibility in polymer blends

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Abstract

A novel use of the process of physical aging has been employed to help distinguish whether the two components of a polymer blend are miscible or immiscible. This approach appears to be particularly useful in the special case where the glass transition temperature of the two respective blend components are relatively close, i.e. 10 to 20°C. This novel approach is demonstrated through the use of blends of racemic polylactide with the optically active L form of the same species. Different molecular weights and their blends were utilized in this study.

Introduction

The use of polymer blends and their preparation has been of increasing interest in both the industrial and academic community. For practical purposes, blends offer the possibility of generating intermediate or possibly quite different properties than those of the components comprising the blend. Of particular interest is understanding, predicting, and making measurements of the miscibility of two polymer components. This is of importance for purposes of better understanding the overall structure-property behavior of the final blend. Many techniques have been developed for determining miscibility as has been discussed by Walsh and Rostami (1). Typically, the principal parameter utilized for measurement is that of the glass transition temperature, T_g . For compatible blends, a single T_g is often closely related to the blend composition through the well known Fox equation which predicts that the final glass transition temperature is a function of the weight fractions of the two polymeric components and their respective homopolymer T_g 's. Additional T_g relationships for blends exist but will not be discussed here (2,3). For incompatible blends containing two homopolymers, two T_g 's are observed which generally are in the same temperature vicinity as where the two pure homopolymer T_g 's are observed unless partial miscibility exists or "stress effects" influence the local thermal properties (4).

A general method for determining T_g is that based on dynamic mechanical spectroscopy. More often, however, the technique of differential scanning calorimetry (DSC) is used. This latter technique is particularly common because of its simplicity and has been widely described and applied in the literature (5,6). However, even this method has limitations or can be possibly misleading in certain cases. In particular, there are two cases that may be of interest where limitations may exist. The first may be in a two phase system containing a relatively small amount of a second component and hence, observation of this component's T_g or the effect of this minor component on the T_g of the more dominant component may not be always easily measured. A second and more interesting case to be addressed here concerns a blend of two homopolymers where their respective T_g 's differ only slightly. In this case, even though

immiscibility may occur, it may be difficult to easily distinguish the two separate T_g 's due to their close proximity. For example, when the difference between the two T_g 's is less than about 10-20°C, it becomes rather difficult to make this separation by thermal analysis -particularly if one is of a minor weight fraction.

The work presented here presents a novel approach to solve this latter particular problem by recognizing the nature of the physical aging process common to glassy materials (7,8,9). Specifically, as has been well discussed in the literature, when an amorphous material is quenched into the glassy state, it is in nonequilibrium form. Depending upon the temperature at which the material is stored below its glass transition region, it will, with time, approach the equilibrium state through the process well known as physical aging. Other terms apply to this same phenomena has been "volume relaxation" and "enthalpy relaxation". Indeed, it is this latter terminology that is of utility here. It has been noted by many authors studying homopolymer systems that the use of enthalpy relaxation is a means for following the process of one index of this kinetic response of the system (7,8,9). The general trend for such physical aging and its associated correlation with the approach to equilibrium is given in Fig. 1 which illustrates the general response often observed by DSC measurements on a quenched material as a function of aging time in the glassy state. This "enthalpy peak" denoted by DSC measurements as a function of aging time (known as sub T_g annealing) can be utilized as a means of accenting a glass transition temperature response as should be obvious. With this in mind, we will now address the application of DSC for following the occurrence of miscibility or immiscibility in blends of polylactide materials, the two components being the L form of polylactide ($T_g = 65^\circ\text{C}$) and the other being the racemic or DL form ($T_g = 53^\circ\text{C}$). While the racemic form is an amorphous material, the L form can crystallize if allowed sufficient time above T_g . However, it can be easily quenched into the glassy state which is the case for all of the systems discussed here.

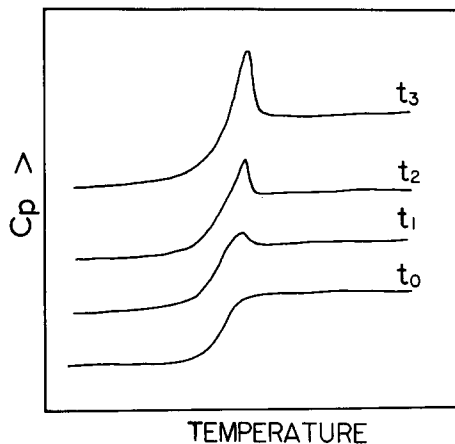


Figure 1: A general series of DSC traces illustrating the general effect of how physical aging influences the glass transition response of a homogeneous system. t_0 represents the DSC scan following quenching into the glassy state whereas all other times refer to DSC traces taken after "sub T_g annealing" in the glassy state where $t_1 < t_2 < t_3$. The curves are vertically shifted for sake of clarity.

Experimental

Materials: The PLA polymers used to prepare the blends were bulk polymerized using stannic octoate as a catalyst and lactic acid as an initiator. The optically active L ionomer species (L-Lactide) was used for the pure L form of the polymer while the optically inactive dimer was used for preparing the racemic (DL) form. The ring opening reactions were performed under vacuum and the conversion was always greater than 95%. The final molecular weights of these polymers were characterized by intrinsic viscosity using the Mark Houwink equation with parameters given by Shindler and Harper (10). After purification, these systems were used to prepare the blends by simultaneously dissolving different amounts of PLA-L and PLA-DL in chloroform and slowly evaporating the solvent at room temperature and then drying the mixture at 70°C for 24 hours. These cast films were then pressed at 200°C for 30 seconds and rapidly quenched to room temperature to obtain glassy transparent starting materials. These systems were then used as the basis for analysis regarding miscibility or immiscibility of the mixtures.

Experimental Techniques: The thermal analysis of these blends were performed on a Perkin-Elmer DSC-4. The weight of the samples utilized was in the range of 10 mg or less. All samples were heated at 20° per minute to 70°C for thirty seconds. Then the samples were rapidly cooled to room temperature where they were stored in the glassy state at 23°C in a desiccator over phosphorus pentoxide for 2,14, and 20 days respectively -the various periods of physical aging utilized. The purpose of the rapid heating to 70°C for all samples was for the purpose of establishing a zero control time when physical aging would be initiated upon cooling from above T_g. Later DSC scans for purposes of denoting the enthalpy peak (DSC) associated with physical aging were obtained by heating at a rate of 20°C per minute. This somewhat rapid rate of heating tends to promote some "overshoot" at the glass transition temperature, however, by using a control, this overshoot effect can be noted and separated from the physical aging process.

Results and Discussion

Figures 2a and b provide DSC scans as a function of physical aging time for the nonblended pure PLA-L homopolymer ($M_v = 290,000$) and that of homopolymer PLA-DL ($M_v = 240,000$) respectively. It is noted that for the homopolymers which differ in their glass transition temperature by about 12 degrees, quickly develop very distinct physical aging peaks due to the fact that the aging process takes place in rather close proximity to the expected glass transition region. Recall that the physical aging process of glasses does occur more rapidly as the sub T_g annealing temperature approaches the glass temperature although the exact rate is somewhat dependent on the polymer type (9). From Fig.2a&b, it is particularly noteworthy just how great the enthalpy peak will develop in its magnitude in such short time scales for these materials.

Turning to blends of the L & DL polymers, Figures 3a and b illustrate comparable aging responses but for blends of these two homopolymers described above but now in the ratio of PLA-L/PLA-DL = 90/10 and 50/50 wt. percent respectively. In the first, which is when the DL component is of minor fraction, the initial DSC scan on a fresh quenched sample shows no real distinct signs of two glass transition temperatures. However, with aging time over the period of 20 days, it becomes very distinct that two glass transition temperatures do occur with their respective enthalpy peaks developing where the respective homopolymer components would lie. Certainly, this blend then displays immiscibility which could have been overlooked had physical aging not been utilized as a means of denoting its occurrence. In Figure 3b which illustrates a 50/50 weight fraction mixture of the L and DL components, these systems do display signs of immiscibility and two glass transitions temperatures even in the freshly quenched material. However, the distinctness of these two glass transition temperatures

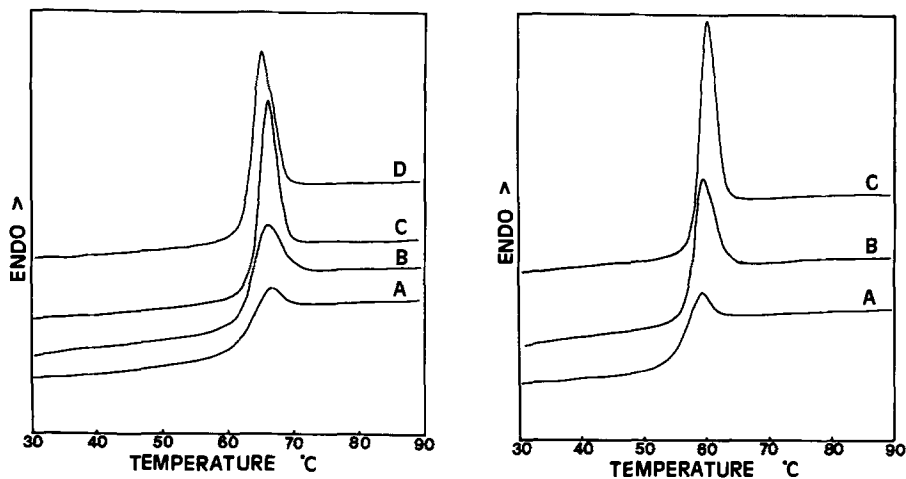


Figure 2: DSC scans as a function of physical aging at 23°C for different times: a) pure PLA-L ($M_v = 290,000$). Aging times = A) 0 days; B) 2 days; C) 14 days and D) 20 days; b) pure PLA-DL ($M_v = 24,000$). Aging times = A) 2 days; B) 14 days; and C) 20 days.

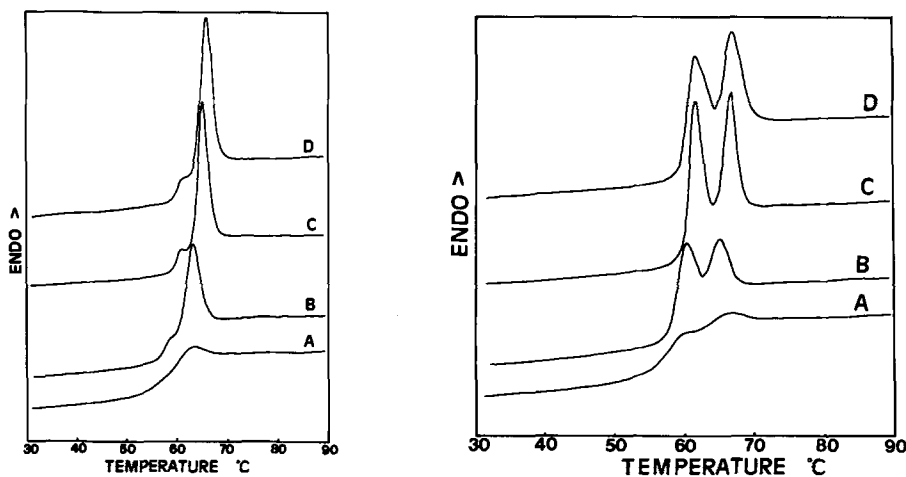


Figure 3: DSC scans following different physical aging times for two different composition ratio blends of PLA-L/PLA-DL having weight percentages of a) 90/10 and b) 50/50 respectively. The M_v values are the same as those given in Figure 2. Aging times = A) 0 days; B) 2 days; C) 14 days; and D) 20 days.

become particularly clear upon physical aging thereby again further establishing the conclusion that immiscibility of these two high molecular weight homopolymers which differ only in terms of their stereoregularity. The observation that mixtures of different configuration or stereoregular forms of a given polymer may display immiscibility is not new for such measurements have been made by more sophisticated investigations utilizing small angle neutron scattering, etc. (11).

Figures 4a&b provides some additional examples of the recognition of immiscibility upon physical aging of lower molecular weight mixtures of PLA-L/PLA-DL. In particular, the data were obtained on blends of homopolymers of 65,000 and 53,000 respectively for these two components at two different composition ratios - 90/10 and 50/50 by weight percent. It can be clearly seen that immiscibility occurs for either blend ratio utilized in this study for these two lower molecular weights. Finally, Figure 5 is presented which shows a final blend of PLA-L/PLA-DL with each component having 65,000 molecular weight. In this series which is shown as a function of aging time, there is only one glass transition temperature observed for the 70/30 blend ratio utilized clearly indicating that miscibility appears to be established at this composition and molecular weight. It should be pointed out that we have carried out additional studies of the crystallization kinetics of these same blends discussed here have also found that at the lowest molecular weights of the two blend components, miscibility occurs for this same range of composition ratios.

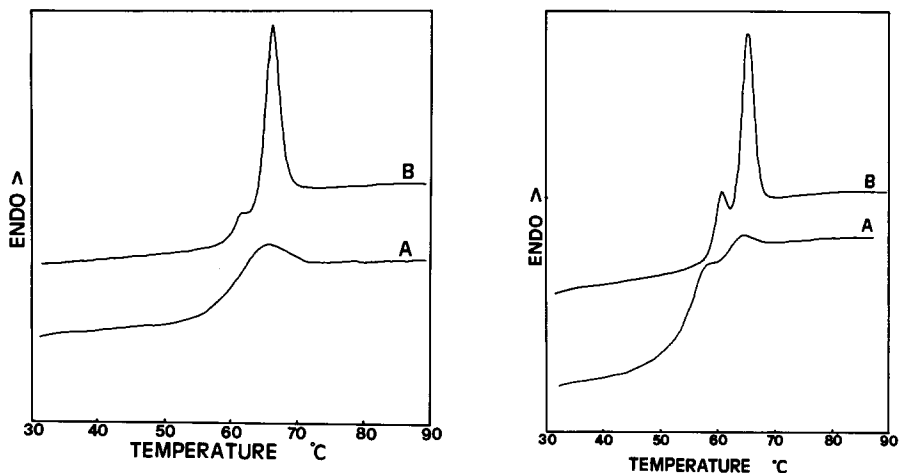


Figure 4: DSC scans as a function of physical aging time obtained on two immiscible blends of PLA-L/PLA-DL materials having homopolymer molecular weights of 65,000 and 53,000 respectively. The composition ratio of PLA-L/PLA-DL is 90/10 in Figure 4a and 50/50 in Figure 4b. The aging times at ambient in Figure 4a and 4b are (A) 0 days, (B) 20 days.

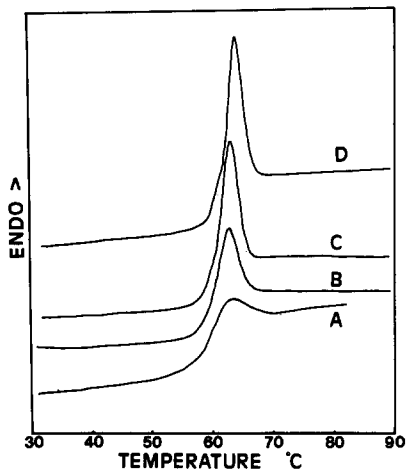


Figure 5: DSC scans as a function of physical aging time for a PLA-L/PLA-DL blend each having its component molecular weight of 65,000. The blend weight ratio is 70/30. Aging time: A) 0 days; B) 2 days; C) 14 days and D) 20 days.

Signs of partial miscibility can also be observed in specific blends - the important variables being composition ratio and molecular weight of the two components. In particular, Figure 6 is presented which illustrates a blend of PLA-L/PLA-DL having respective molecular weights of 530,000 and 65,000 respectively and where the blend ratio by weight is 50/50. Also shown in the same figure are the respective DSC responses of the individual homopolymers aged for the same time periods utilized for the blend. While somewhat indirect in nature, the data indicate that there appears to be partial miscibility of the two components due to the fact that the "enthalpy enhanced" T_g peaks of the blend are intermediate between the respective enthalpy peaks of the two pure homopolymers. That is, these results suggest that there may well be some partial miscibility of one component in that of the other. We would not wish to absolutely conclude that this difference in placement of the enthalpy peaks is a direct indicator of partial miscibility but it is certainly suggestive of this speculation.

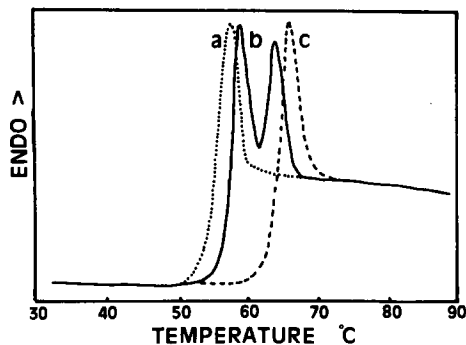


Figure 6: DSC traces of three materials that have been physically aged for 20 days: A) homopolymer PLA-L of 530,000 molecular weight; B) a blend of these two systems of 50/50 weight ratio and C) PLA-DL homopolymer of 65,000 molecular weight.

In summary of the work presented here, it has been clearly demonstrated that physical aging can at least be utilized as a simple means of denoting immiscibility in blends containing homopolymers possessing somewhat similar glass transition temperatures.

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