



## Test method

## Determination of ultra-low glass transition temperature via differential scanning calorimetry

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## ABSTRACT

A novel method was developed to determine the ultra-low glass transition temperature ( $T_g$ ) of materials through physical blending via differential scanning calorimetry. According to the Fox equation for polymer blends, a blend of two fully compatible polymers has only one  $T_g$ . The single  $T_g$  is a function of the  $T_g$ s of the two simple polymers. Thus, the ultra-low  $T_g$  of one material can be obtained from the  $T_g$ s of another polymer and their blends. The error of  $T_g$  measurements depends on the measurement error of the  $T_g$ s for the blends and another polymer. The method was successfully applied to determine the  $T_g$ s of acetyl tributyl citrate (ATBC), tributyl citrate (TBC) and poly(ethylene glycol)s (PEG)s with different molecular weights. The  $T_g$ s for ATBC, TBC, PEG-4000 and PEG-800 were  $-57.0$  °C,  $-62.7$  °C,  $-76.6$  °C and  $-83.1$  °C, respectively. For all the samples, the standard deviation of measurements was less than  $3.3$  °C, and the absolute error of measurements was theoretically not more than  $5.3$  °C. These results indicate that this method has acceptable precision and accuracy.

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## 1. Introduction

The glass transition temperature ( $T_g$ ) is described as the change in temperature in which a reversible transition occurs in amorphous materials (or in amorphous regions within semi-crystalline materials) from a hard and relatively brittle state to a molten or rubber-like state. An amorphous material below its  $T_g$  (glassy state) behaves like a brittle solid but without a crystalline structure and only has short-range order. When a plastic undergoes the glass transition, many of its physical properties, especially mechanical properties, change very rapidly. The modulus

changes by three to four orders of magnitude because the transition temperature occurs within the range of only a few degrees Celsius. Thus, the material suddenly turns into a soft elastomer from a hard solid, and its applied performance changes completely. Specific polymers that behave like rubbers are normally used above their  $T_g$ s, and those that behave as plastics are used below their  $T_g$ s. Polymers that are used as plastics lose their plastic performance and change into rubbery materials when the temperature exceeds their  $T_g$ s. Materials used as rubbers lose their high flexibility and become hard and brittle plastics when the temperature is decreased below their  $T_g$ s. Thus,  $T_g$  is an important characteristic parameter of polymers in theory and practice.

$T_g$  can be determined by various techniques, such as dynamic mechanical analysis (DMA), differential thermal analysis (DTA), differential scanning calorimetry (DSC)

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[1,2], synchronous scan spectra (SSS) [3], IR spectroscopy [4–6], nuclear magnetic resonance (NMR) [7,8], electron spin resonance (ESR) [9], dilatometry, dielectric relaxation [10] and inverse gas chromatography [11,12]. DSC and DMA are usually performed to determine  $T_g$  from a very low temperature, such as  $-170$  °C for DSC 6220 (Seiko Instruments, Inc., Japan) and  $-190$  °C for DMA 8000 (PerkinElmer). Thus, in theory, the  $T_g$  values obtained directly from DSC and DMA are above  $-140$  °C and  $-160$  °C, respectively. However, the  $T_g$ s of particular materials cannot be directly measured because they cannot form an amorphous region. This inability to form an amorphous region is due to the high crystallization of these materials, even if they are quenched at a very high cooling rate from their molten state, or because their  $T_g$ s may be too low to be detected by instruments. By blending with another polymer, the crystallization capacity of a crystalline component may be inhibited and the component can form an amorphous region. Thus, its  $T_g$  can be obtained from polymer blending. By blending a material for lower  $T_g$  with another compatible polymer, the single  $T_g$  of blends is within the range of the detection limit of the instrument, and a lower  $T_g$  for the component can be obtained according to the Fox equation for polymer blends. Thus, this method can measure not only the  $T_g$ s of crystalline polymers but also ultra-low  $T_g$ s, where the temperatures greatly exceed the detection range of instruments. The determination of ultra-low  $T_g$ s of materials may be applied in low-temperature technology. Furthermore, the ultra-low  $T_g$ s of materials such as plasticizers can be measured to estimate the  $T_g$ s for its blends with other compatible polymers.

For the binary blends of poly(lactic acid) (PLA) and poly(ethylene glycol) (PEG) or poly(ethylene oxide) (PEO), Nijienhuis et al. [13] reported that all blends containing up to 50 wt% PEO showed a single  $T_g$ , and the equilibrium melting points of PLA in these blends decreased with increasing PEO fractions, which suggested that PLA and PEO were compatible in the amorphous phase. Sheth et al. [14] concluded from DSC results that the miscibility of the PLA/PEG blends depended on the PEG concentration, and that PEG and PLA formed miscible blends in compositions less than 50/50.

The determination of  $T_g$  of PEG or PEO has been investigated using various techniques. Faucher et al. [8] obtained  $T_g$  for PEG-6000 ( $-53$  °C) by mechanical loss and by broadline NMR. Yohei [9] obtained  $T_g$  for PEG-4000 ( $-52$  °C) by ESR. Vaia et al. [15] and Cruickshank et al. [16] obtained  $T_g$  values for PEO-100,000 ( $-55$  °C) and PEG-300 ( $-77$  °C) via DSC. Törmälä [17] measured  $T_g$  of PEG by a spin-probe technique. PEGs with molecular weights of 3,000 g/mol to 22,000 g/mol had  $T_g$  of  $-60$  °C, which was independent of molecular weight. All the results obtained by direct measurements are usually higher than the actual values because of the high crystallizability of PEGs or PEOs [8].

In the present work, we studied PLA blends with PEG, acetyl tributyl citrate (ATBC) and tributyl citrate (TBC) via DSC. The  $T_g$ s of PEG, ATBC and TBC were successfully determined according to the Fox equation. Until now,  $T_g$  measurements for plasticizers, such as ATBC and TBC, have not been reported. The precision and accuracy of the results were evaluated by experimental data and theory.

## 2. Experimental section

### 2.1. Materials

Amorphous PLA with  $M_n = 9.9 \times 10^4$  g/mol and  $M_w = 1.53 \times 10^5$  g/mol was manufactured by Zhejiang Hisun Biomaterials Co., Ltd., Taizhou, Zhejiang, China. PEGs, including PEG-4000 and PEG-800, were purchased from Aladdin Chemistry Co. Ltd (Shanghai). Dichloromethane (DCM, analytical reagent) was produced in China. ATBC (LMFLEX<sup>®</sup> LM40, 99%) and TBC (LMFLEX<sup>®</sup> LM30, 99%) were obtained from Jiangsu Lemon Chemical & Technology Co., Ltd., Yixing, Jiangsu, China.

### 2.2. Sample preparation

PLA and PEG were dried in high vacuum conditions for 4 h at 90 °C and 120 °C, respectively. ATBC and TBC were used directly without further purification. The PLA blends containing PEG, ATBC or TBC with total weight of 1.0 g were dissolved in an appropriate amount of DCM at various ratios, i.e., PLA/PEG (ATBC, TBC) = 100/0, 95/5, 90/10, 85/15, 80/20, 75/25 and 70/30 in weight fraction. The solvent was then carefully evaporated to make PLA blend films for DSC analysis.

### 2.3. Measurements

DSC analysis was implemented on a TA DSC-Q10 in a nitrogen atmosphere. The weight of samples, which were placed in an aluminum pan, was 5 mg to 10 mg. The samples were heated to 190 °C at 10 °C/min and held at 190 °C for 5 min to eliminate any thermal history. The samples were then quenched to  $-80$  °C and finally reheated to 190 °C at a rate of 10 °C/min. The reheating scans were recorded.

## 3. Results and discussion

The change in  $T_g$ s of binary blends mainly depends on the compatibility of the two components. The  $T_g$ s of binary blends with different degrees of compatibility are shown in Fig. 1. If the two components are completely incompatible with each other, then they have two  $T_g$ s that correspond to the two components. If the two components are partially compatible, then the blends have two  $T_g$ s shifted towards each other when the compositions of blends are out of the range of compatibility. If the compositions are in the range of compatibility, such as a component at low levels, the blends have a single  $T_g$ . If the components in binary blends are fully compatible, then the blends display a single  $T_g$  within the full range of compositions. However, when a single  $T_g$  for a binary blend is present, intuitively evaluating the compatibility of the two components is sometimes difficult because the  $T_g$  of a component could not be detected due to its low content or is beyond the instrument detection limit.

According to the theory of polymer blends, a blend of fully compatible binary polymers has only one  $T_g$ , which is in line with the Fox equation, as shown in Eq. (1).

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