Effect of a Low Molecular Weight Plasticizer on the Thermal and Viscoelastic Properties of Miscible Blends of Bacterial Poly(3-hydroxybutyrate) with Cellulose Acetate Butyrate

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ABSTRACT: Blends obtained by melt compounding poly(3-hydroxybutyrate) (PHB) with cellulose acetate butyrate (CAB, $DS_{Bu} = 2.50$; $DS_{Ac} = 0.18$) are found to be miscible over the whole composition range by both calorimetry (DSC) and dynamic mechanical spectroscopy (DMTA). In the range of PHB contents from 0 to 50% the blend glass transition temperature (T_g) strongly depends on composition (in excellent agreement with the predictions of Wood's equation), while a much less substantial dependence is found when the amount of PHB exceeds 50%. In the former composition range, in addition to the strongly composition-dependent T_g, another relaxation associated with mobilization of the low-T_g component is observed at a lower temperature. The plasticizer di-*n*-butyl phthalate (DBP) is miscible in all proportions with both CAB and PHB. Analogous to the polymeric CAB/PHB blends, the two polymer/diluent systems investigated (CAB/DBP and PHB/DBP) show a dual dependence of T_g on composition. In binary mixtures such behavior appears to be independent of the macromolecular or low molecular weight nature of the low-T_g component. Addition of a fixed amount of DBP plasticizer to CAB/PHB blends with varying composition (PHB content from 0 to 100%) causes a significant decrease of T_g of the binary polymer blends; the T_g depression is larger the higher the amount of DBP in the ternary blend. Concomitant with the expected "plasticizing" effect on T_g, the presence of DBP also induces a decrease in the characteristic temperature of the additional low-temperature transition observed in CAB/PHB blends. In the ternary blends, the temperature of such a transition is a function of DBP content only, being independent of the relative amount of the two polymers (CAB and PHB).

Introduction

Recently, intensive fundamental and applied research has been devoted to the study of bacterial poly(3-hydroxybutyrate) (PHB) and the related poly(hydroxyalkanoate)s (PHA).[1-4] The practical interest in PHB is mainly associated with properties such as biocompatibility, which favors its use in the biomedical field, and biodegradability in the environment, which has attracted much attention in connection with waste management issues. In this latter case, a problem which needs to be solved before envisaging wide-scale applications is the high production cost of bacterial polymers. An indirect means to lower cost is polymer blending: moreover, when two polymers form miscible blends, materials with a broad range of properties regulated by blend composition can be obtained. It has been recently shown[5,6] that both PHB and a bacterial 3-hydroxybutyrate/3-hydroxyvalerate copolymer, P(3HB-*co*-3HV) containing 20 mol % of 3HV units, are miscible in the melt over the whole composition range with some cellulose esters (CE). In these blends, PHB, whose glass transition temperature (T_g) is ca. 0 °C, acts as a high molecular weight plasticizer toward the high-T_g cellulose derivatives. As a consequence, the blends exhibit a composition-dependent glass transition, in excellent agreement with the behavior predicted for totally miscible binary systems.[7,8] Miscibility causes changes in the broadness of the window between T_g and the melting temperature (T_m), thus affecting the capability of the bacterial polymer as well as the cellulose derivative to crystallize out of the homogeneously mixed blend at $T > T_g$.

The present work investigates the thermal and viscoelastic properties of a ternary system obtained through the addition of a low molecular weight plasticizer to PHB/CE blends of varying composition. To avoid the morphological complexity of blends where both components are crystallizable, an amorphous cellulose acetobutyrate (CAB) which did not crystallize in any of the experimental conditions employed was used. One of the main problems with PHB processing is poor thermal stability at temperatures slightly higher than the melting temperature (T_m), and a procedure commonly adopted to widen the polymer processability window is plasticization. The plasticizer selected (di-*n*-butyl phthalate (DBP)) is reported to be biodegradable[9] and appears to be suitable as an additive for blends with potential uses as new biodegradable materials. Preliminary to the study of the ternary system, miscibility of PHB with the selected CAB as well as of the low molecular weight diluent with each polymeric component has been investigated.

Experimental Section

Materials. Poly(3-hydroxybutyrate) (PHB, BXGV9, M_n = 350000, M_w = 1140000) was kindly supplied by ICI Biological Products (U.K.). Cellulose acetate butyrate was an Eastman Kodak product (CAB 531-1) whose degree of substitution (DS_{Bu} = 2.50, DS_{Ac} = 0.18) and molecular weight (M_n = 71600, M_w = 161000) were kindly determined by Dr. C. Buchanan, Eastman Chemical Co., Kingsport, TN. Di-*n*-butyl phthalate (purity > 99%) was synthesized as previously reported.[10]

Preparation of Polymer/Plasticizer Blends. Mixtures of DBP with CAB or PHB in different weight ratios covering the whole range of compositions were prepared by weighing appropriate amounts of the components directly in the DSC pans. According to a procedure previously described,[11] polymer–diluent equilibrium mixing was obtained by heating the sealed pans in the DSC up to 210 °C followed by rapid cooling to low temperature. The excellent reproducibility of subsequent DSC scans attested to both the attained equilibrium and the absence of any appreciable molecular weight decrease due to thermal degradation.

Preparation of Polymer/Polymer Blends. Blends of PHB and CAB with different weight ratios were obtained by melt mixing the blend components for 1.5 min at 195 °C in a

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noncommercial miniature mixing–injection molding machine (the amount for each mixing–injection molding operation was 0.6–0.8 g). The blends were molded into small bars (30 mm × 7.5 mm × 1.5 mm), quenched in an ice–water mixture, and allowed to age at room temperature (22–28 °C) for at least 3 weeks. Specimens of all compositions were transparent immediately after quenching from the melt but, upon room storage, blends with PHB contents higher than 50% turned opaque, due to PHB crystallization. Prior to DMTA measurements, such blends were stored in a refrigerator (–10 °C) after melt quenching to prevent PHB crystallization.

Preparation of Ternary Blends. Ternary blends were prepared according to the following procedure: (1) dry blending of the appropriate weight ratios of liquid DBP plasticizer with the pure polymers (PHB and CAB) in powder form at 100 °C for 30 min; (2) melt mixing and injection molding at the same temperature (195 °C) as the binary CAB/PHB blends. The small molded bars were quenched into an ice–water mixture and stored at room temperature. While the weight ratio of the two polymers varied from 0 to 1, the plasticizer amount remained fixed: the DBP content, calculated as $\text{weight}_{\text{DBP}}/\text{weight}_{\text{PHB+CAB}}$, was 0.08 and 0.15 and will be indicated as 8 and 15 phr, respectively, throughout the text.

Experimental Methods. Dynamic mechanical measurements were performed with a DMTA (Polymer Laboratories Ltd.) operated in the dual cantilever bending mode at a frequency of 3 Hz and a heating rate of 3 °C/min over the temperature range -50 to +150 °C. Calorimetric (DSC) measurements were carried out by means of a DuPont 9900 thermal analyzer; the temperature scale was calibrated with high-purity standards (*n*-heptane, *n*-octane, benzene, lauric acid, and indium). After preliminary heating to 215 °C to cancel the previous thermal history, followed by rapid quenching to –150 °C, DSC scans were performed at 20 °C/min in the range –150 to +215 °C. The glass transition temperature (T_g) was taken at the midpoint ($^1/_2\Delta C_p$) of the stepwise increase of the specific heat associated with the transition.

Results and Discussion

Polymer/Plasticizer Mixtures. DBP is a member of the family of phthalate plasticizers commonly used with cellulose esters for practical applications.[12] The effect of increasing amounts of DBP on the calorimetric glass transition temperature of CAB is shown in Figure 1, together with the T_g behavior of mixtures of DBP with bacterial PHB for the sake of comparison. The latter system has already been reported[11] to be miscible over the whole range of compositions, DBP behaving as a very good plasticizer for the bacterial polymer. The curves drawn in Figure 1 have been calculated according to Wood's[8] equation:

$$T_g = (w_1T_{g1} + kw_2T_{g2})/(w_1 + kw_2) \qquad (1)$$

where w_1 and w_2 are the weight fractions and T_{g1} and T_{g2} the glass transition temperatures of DBP and of the polymeric component, respectively. T_g is the glass transition temperature of the mixture, and k is an empirical adjustable parameter (k = 0.68 and 0.76 for CAB/DBP and PHB/DBP, respectively). Equation 1 is one of the well-known relationships[7,8,13,14] used to describe the T_g–composition dependence in plasticized polymers and in miscible polymer blends.

The results plotted in Figure 1 show that the T_g of CAB is strongly depressed as a consequence of DBP addition: 35% of plasticizer induces a 100 °C decrease of the glass transition temperature. The excellent fit of eq 1 to the experimental T_g data in the range of DBP contents from 0 to 35% indicates that the diluent is evenly dispersed into the polymer and that homogeneous mixtures are obtained. Quite interestingly and in agreement with previous findings for a number of polymer/diluent systems,[11,15–19] including the PHB/DBP mixtures whose T_gs are reported in Figure 1, the mixtures of CAB with high amounts of DBP have a T_g which depends on composition much less than predicted by eq 1. Moreover, in the intermediate range of compositions (DBP contents 35–40%), CAB/DBP mixtures exhibit two glass transitions (see the relevant T_gs in Figure 1). This feature is not peculiar to the system under investigation, having been previously observed in several plasticized polymer system[15–17,19] by means of various experimental techniques including dynamic mechanical and dielectric spectroscopies. As regards DSC, it has been previously reported that a necessary—though not sufficient—condition to obtain individual resolution of the two glass transition phenomena is that the T_gs of the polymer and diluent are far enough apart;[18] otherwise, an apparently single, very broad glass transition at intermediate compositions is observed. Besides the T_g difference, a major role in allowing detection of the two mobilization processes is played by parameters such as intrinsic mobility and width of the relaxation time distribution at the glass transition of each component of the mixture, as well as sensitivity of the specific experimental technique employed and scale of molecular motions sensed.

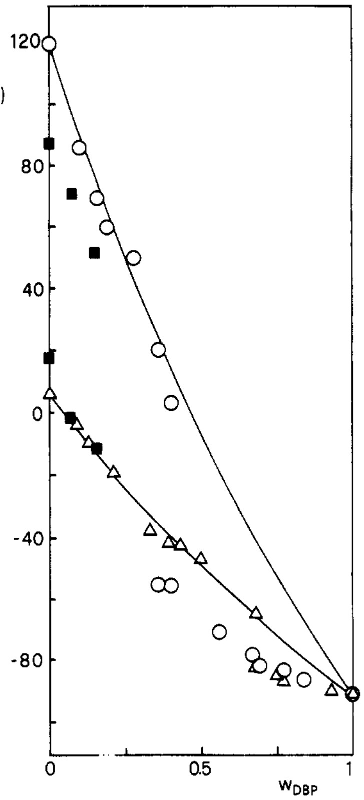

Figure 1. Effect of DBP weight fraction on the glass transition temperature of (○) CAB, (△) PHB, and (■) 80CAB/20PHB blend.

The view that the behavior just described does not result from phase separation associated with the presence of a miscibility gap has recently gained wide acceptance. Increasing experimental evidence and theoretical justification have been made available[20,21] regarding both modification of polymer segmental relaxation due to the presence of solvent and changes of solvent relaxation caused by dissolved polymer. Accordingly, the two glass transition phenomena exhibited by CAB–DBP mixtures indicate, on the one hand, the onset of the cooperative segmental motions of the polymer promoted by the plasticizing effect of the mobile diluent (higher temperature, strongly composition-dependent T_g) and, on the other hand, mobilization of the diluent, slightly hindered by the presence of the dissolved macromolecules (lower

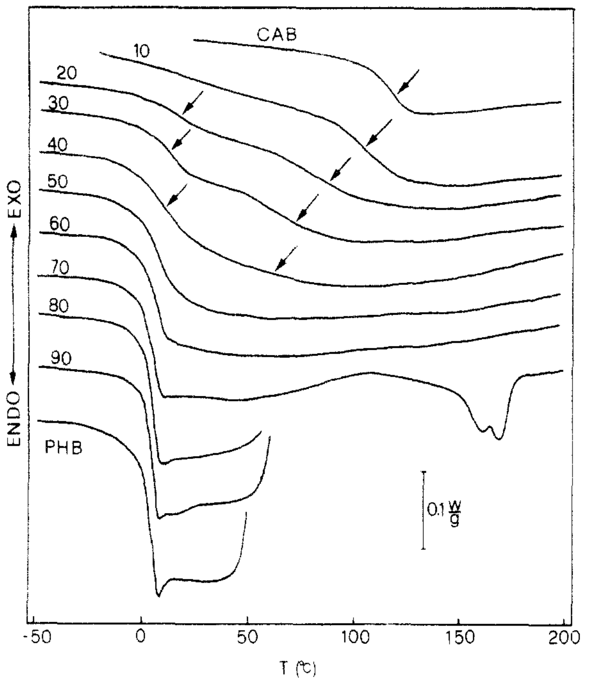

Figure 2. DSC curves of melt-quenched CAB/PHB blends with different PHB weight percents (numbers on curves).

temperature, weakly composition-dependent T_g).

The T_g/composition behaviors reported in Figure 1 show that the glass transition of CAB depends on DBP content more strongly than that of PHB, this effect being clearly related to the larger T_g difference between polymer and diluent in the former case. Conversely, it is worth noting that, notwithstanding the large difference of T_g (ca. 120 °C) and therefore of intrinsic mobility of the two polymers considered, no appreciable differences are observed as regards the low-temperature process associated with mobilization of DBP in the two polymer/DBP systems.

Binary Polymer Blends. The polymers (CAB and PHB) whose plasticization behavior has been discussed above have been used to obtain binary blends with compositions spanning the whole range, from pure CAB to pure PHB. Figure 2 shows the DSC curves of CAB/PHB blends with different compositions together with the curves of the pure blend components. The behavior closely resembles that previously reported for other binary blends of cellulose esters with PHB[5] and P(3HB-*co*-3HV).[6] The glass transition of CAB, evidenced by a step increase in the specific heat (ΔC_p = 0.31 J/(g K), T_g = 119 °C), is seen to shift to lower temperatures with increasing PHB content, while another T_g-like phenomenon appears in a lower temperature range. The temperature location of the latter relaxation also shifts toward lower temperatures—though at a lower rate than the former—and the phenomenon intensifies with increasing PHB content in the blend. When PHB amounts to 50% or more of the total blend weight, only one glass transition phenomenon is detected in the DSC curves, whose temperature and intensity show little change with blend composition. At PHB contents ≥70% an exothermal process appears in the DSC curves above the glass transition (omitted in the truncated curves for the sake of clarity), associated with crystallization of PHB and followed by melting.

The viscoelastic spectra of CAB/PHB blends, maintained in the amorphous state prior to measurement, are shown in Figure 3. The glass transition relaxation of the cellulose ester, indicated by a 3 order of magnitude drop of the elastic storage modulus (E') and a concomitant strong peak in the loss factor (tan δ), is seen to occur at decreasing temperatures with increasing PHB content in the blend. The 50/50 blend clearly shows an increase of the elastic modulus above the glass transition, indicative of sample stiffening caused by PHB crystallization. This phenomenon becomes increasingly evident in blends richer in PHB, where crystallization of the bacterial polymer is promoted by widening of the crystallization window ($T_m - T_g$). In agreement with the DSC results of Figure 2, Figure 3 shows that the temperature location of the glass transition relaxation of blends containing 60–90% PHB only slightly depends on composition.

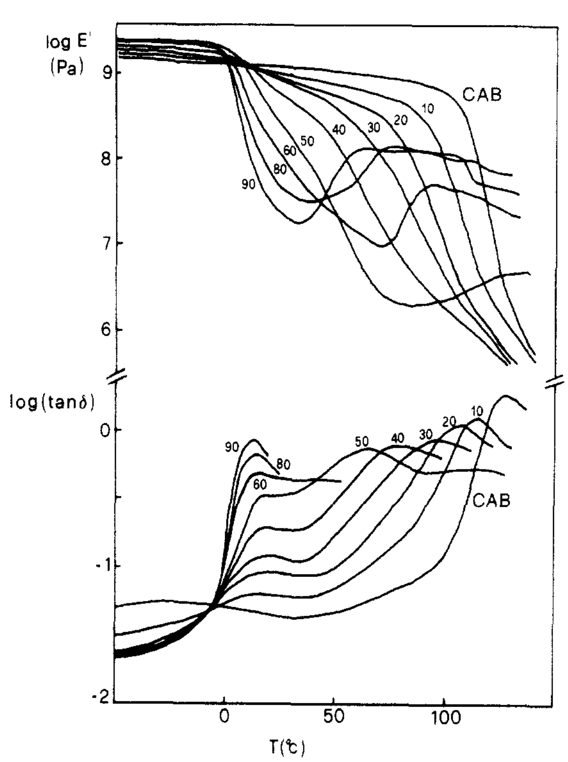

Figure 3. Dynamic mechanical spectra of amorphous CAB/PHB blends with different PHB weight percents (numbers on curves).

It is interesting to note that in the temperature range where PHB-rich blends show the glass transition, also CAB-rich blends show a relaxation phenomenon in the DMTA spectrum, whose intensity increases with increasing PHB content. The glass transition relaxation of blends with 60–90% PHB can therefore be regarded as resulting from the evolution of a relaxation process present in all CAB/PHB blends and assigned to mobilization of the low-T_g component.

When the glass transition temperature of CAB/PHB blends (by both DSC and DMTA) is compared with the predictions of eq 1, a very good fit is obtained in the range of PHB contents from 0 to 40%. This result strongly suggests that mixing of CAB and PHB macromolecules at the segmental level is achieved. Concomitant with this glass transition phenomenon, both DSC and DMTA reveal at a lower temperature the onset of mobility of the low-T_g component, much in the same way as mobilization of the low molecular weight plasticizer is observed in the plasticized polymer systems of Figure 1. It turns out that a common behavior is shown by binary miscible systems, irrespective of the macromolecular or low molecular weight nature of the low-T_g component.

Evidence of two mobilization processes in morphologically homogeneous polymer blends is appearing with growing frequency in the literature[5,6,22–24] and is assigned to "dynamic heterogeneity".[23] This implies that the occurrence of a T_g-like phenomenon related to mobilization

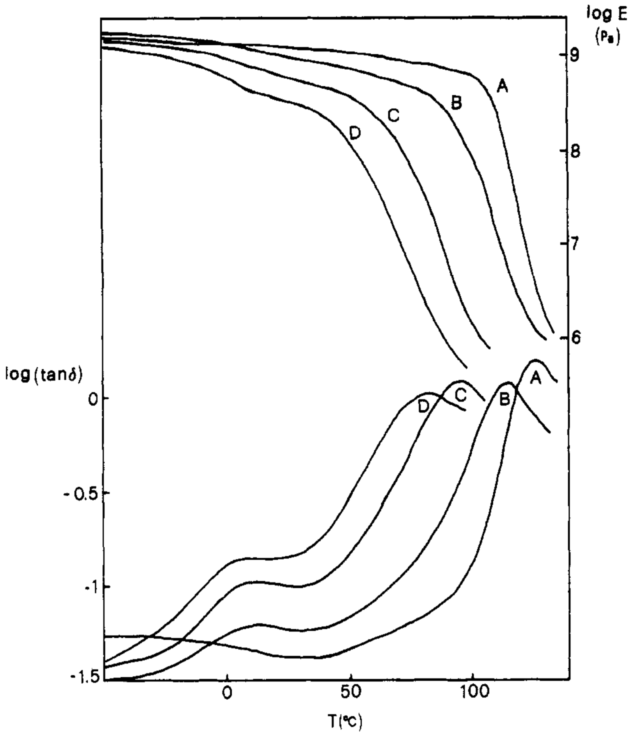

Figure 4. Dynamic mechanical spectra of CAB (A) and of 90CAB/10PHB blend containing 0 (B), 8 (C), and 15 phr (D) DBP.

of the low-T_g component does not conflict with the assumption that the system is a single-phase mixture.

The results of Figure 3 show that the overall mechanical response of CAB/PHB amorphous blends is practically dictated by mobilization of the major component in the blend: CAB in the range of PHB contents from 0 to 50%, and the bacterial polymer at PHB contents higher than 50%. In other words, the transition from the glassy to the rubbery state of the blend material is associated with either the high- or the low-temperature mobilization process, depending on the content of the respective high- and low-T_g component in the blend.

Ternary Blends. The effect of the addition of the common plasticizer DBP to CAB/PHB blends has been investigated over a range of plasticizer concentrations of practical interest, i.e., low enough to avoid volatilization of the low molecular weight substance during melt processing of the ternary blends as well as exudation upon storage. Figure 4 compares the dynamic mechanical spectra of pure CAB with those of the binary 90CAB/10PHB blend and of the ternary system obtained through addition of 8 or 15 phr or DBP plasticizer to the binary polymer blend. Observation of the temperature location of the modulus drop and of the corresponding tan δ peak for the one-, two-, and three-component systems reported suggests that the result of the addition of the low molecular weight plasticizer (see curves C and D) is to enhance the plasticizing effect displayed by the bacterial polymer (compare curve B with curve A). In other words, while PHB behaves like a high molecular weight plasticizer by decreasing the glass transition of CAB, increasing amounts of DBP further decrease the T_g of the CAB/PHB blend. DBP also affects the low-temperature part of the dynamic mechanical spectrum of the 90CAB/10PHB blend, which, concomitant with the disappearance of the secondary relaxation of pure CAB (partially visible in Figure 4 below 0 °C), shows a relaxation associated with PHB mobilization, already discussed in connection with Figure 3. Such a relaxation is seen to shift to lower temperature and strengthen with increasing DBP content.

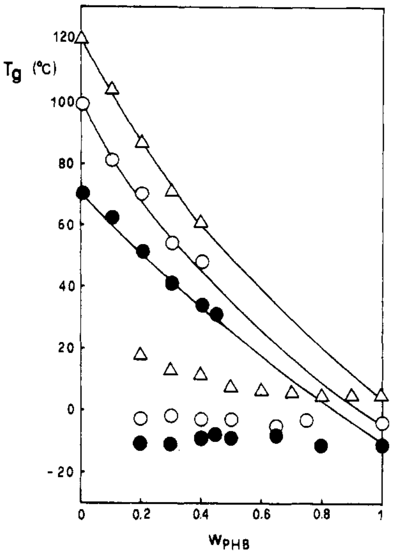

Figure 5. Dependence of T_g on PHB content for (△) CAB/PHB, (○) CAB/PHB + 8 phr DBP, and (●) CAB/PHB + 15 phr DBP.

The behavior illustrated in Figure 4 for one of the binary blends (90CAB/10PHB) is representative of the general response of CAB/PHB blends to the incorporation of DBP plasticizer. Figure 5 summarizes the DSC results obtained for the various ternary blends investigated, which were obtained through addition of a constant amount of DBP plasticizer to the whole series of varying composition CAB/PHB blends. It is quite evident that both mobilization processes shown by the CAP/PHB system are affected by the presence of DBP plasticizer. In the first place, the composition-dependent T_g of the binary blends, which is satisfactorily fitted by eq 1 with $k = 0.63$, is progressively depressed by the addition of increasing amounts of DBP, the ternary blends showing a dependence of T_g on PHB content which is again closely fitted by eq 1 (see curves in Figure 5, with $k = 0.60$ and 0.85 for ternary blends containing 8 and 15 phr DBP, respectively). Secondly, it is interesting to note that the addition of DBP plasticizer practically cancels the slight dependence of the low-temperature transition on CAB content, observed in binary CAB/PHB blends. As a matter of fact, the mobilization process associated with PHB in ternary blends occurs at a temperature which is lower the higher the DBP content (compare data for blends with 8 and 15 phr DBP) but is invariant with the amount of CAB in the blend and corresponds to the T_g of pure PHB containing the appropriate amount (8 or 15 phr) of DBP plasticizer. Keeping in mind that the glass transition temperature of DBP is −91 °C and that PHB mobilization occurs at a much higher temperature, the above observation indicates that the constraints to segmental mobilization of PHB imposed in the binary blends by the high-T_g CAB component are suppressed in ternary blends by the presence of the highly mobile DBP molecules. Apart from the presence of the latter low-temperature relaxation, which is typical of binary blends, the results discussed above concur to suggest that the low molecular weight plasticizer behaves toward the miscible CAB/PHB blend system much in the same way as when it plasticizes a single-component, pure polymer. To further confirm this point, T_g data illustrating the effect of DBP addition to one of the binary CAB/PHB blends taken as an example (80CAB/20PHB) have been plotted in Figure 1 (full symbols). In the range of DBP contents explored, the glass transition of the binary blend (T_g = 87 °C) is seen to decrease with increasing plasticizer content (T_g = 70 and 51 °C when

DBP is 8 and 15 phr, respectively) with a trend which closely mimics the behavior of plasticized plain CAB, shown in the same figure. This results suggests that the plasticizer "sees" the polymeric 80CAB/20PHB blend as if it were a single pure polymer with the pertinent T_g.

For the blend in question, Figure 1 also shows how the characteristic temperature of the low-temperature mobilization process ($T = 18$ °C for 80CAB/20PHB) is affected by DBP addition. As already mentioned in connection with Figure 5, DBP facilitates the onset of segmental mobility of the bacterial polymer in the ternary blend: not only does the hindering effect of the high-T_g CAB component disappear but also the characteristic temperature of the transition drops to match the T_g/DBP content dependence of plain PHB. This finding should not induce the erroneous idea that a hypothetical pure-PHB phase is undergoing plasticization by DBP: suffice it to observe in Figure 5 that a fixed amount of DBP produces an identical effect on the low-temperature mobilization process of blends containing widely different amounts of PHB (from 20 to 80%).

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