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Influence of dibutyl phthalate on the mechanical, thermal, and relaxation behaviour of poly(methyl methacrylate) for denture-base soft liners

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Methyl methacrylate and six solutions of methyl methacrylate/dibutyl phthalate (nominally 5 to 30% v/v) were polymerized into thin sheets using gamma radiation. Dynamic mechanical spectra of the storage modulus, loss modulus and loss tangent, as well as changes in length, were investigated as a function of temperature. From these measurements, the depression of the storage modulus and glass-transition temperature were obtained. Subsequently, differential scanning calorimetry (DSC) and cross-polarization-magic-angle-spinning NMR were used to obtain additional glass-transition and relaxation-time measurements. Based upon these experiments, a specific form of the rule of mixtures described the depression of the glass-transition temperature. From storage-modulus measurements, antiplasticization was evidenced at very low temperatures and at compositions greater than 25% v/v. Solid-state NMR confirmed that plasticization causes an increase in polymer main-chain motion via the physical loosening of secondary bonds between polymer chains.

1. Introduction

The depression of the glass-transition temperature of a linear polymer by a diluent can generally be explained by free-volume [1–3] or by thermodynamic theories [3–8]. The adequacy of the free-volume theory is often explained using Kelley's and Bueche's treatment for the system, poly(methyl methacrylate)/diethyl phthalate (PMMA/DEP) [9–11]. Recent workers, who have studied the PMMA/DEP and PMMA/dioctyl phthalate (DOP) systems, found it necessary to postulate negligible changes in volume on mixing in order to account for the simple behaviour of the Kelly and Bueche theory [12].

In 1950, Nielsen *et al.* [13] showed that mechanical and electrical properties of many plasticized polymer systems could be predicted over a range of temperatures, if the low-frequency transition temperatures of both constituents were known. From dynamic tests, this transition could be defined as the temperature at which the low-frequency mechanical damping was at a maximum or where the logarithm of the elastic modulus plotted against temperature exhibited an inflection point. The latter corresponded to the temperature at which the polymer was transformed from a rigid to a rubbery material. In most compatible plasticized polymer systems, such a transition followed a simple relationship with volume or the weight fraction, provided that the empirical constant relating volume-expansion coefficients below and above the glass-transition temperature equalled one or two, respectively.

When certain low-molecular-weight materials such as plasticizers are added to glassy polymers, main-chain motions increase proportionally with the plasticizer content. As a consequence, the mechanical properties of polymers are affected. Since plasticizers can also lower the glass-transition temperature of polymers, the physical loosening of bonds, which occurs as a consequence of increased segmental mobility by a plasticizer, might be investigated. The present work quantifies the effects of a plasticizer on the glass-transition temperature, T_g, the storage modulus, E', and relaxation times, $T_{1\rho}$ in order to help design plasticized polymers that are commonly used in biomedical applications – particularly denture-base soft liners.

2. Experimental procedure

Solutions were made of methyl methacrylate monomer (MMA) and dibutyl phthalate plasticizer (DBP)

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(both from the Aldrich Chemical Co., Milwaukee, WI, USA). Seven ratios of monomer and plasticizer (nominally 0, 5, 10, 15, 20, 25 and 30% v/v) were polymerized by 6 h exposure to a ^{137}Cs gamma-ray source (dose rate $\approx 0.6 \times 10^6$ rad h^{-1}, ambient temperature = 35 °C) in a nitrogen atmosphere. Samples for dynamic mechanical analysis were prepared by confining the MMA/DBP solutions between glass microscope slides that were bounded by a window frame of polytetrafluoroethylene. After these sheets were polymerized, samples were cut and sanded into strips of dimensions 7.0 × 0.4 × 0.07 cm.

The dynamic mechanical analysis (DMA) was performed with an Autovibron DDV-II-C at the most commonly reported strain frequency of 11 Hz [14]. Samples were scanned at 2.0–2.5 °C min^{-1} from − 150 °C to a point above their T_g at which the Autovibron could no longer maintain adequate tension on the specimen. Plots of storage modulus, E', loss modulus E'', loss tangent, $\tan\delta = E''/E'$, and change in length, Δl were generated as a function of temperature, T. The T_g is taken as the change in slope by intersecting tangents of the E' versus T plot and the Δl versus T plot [15]. These two estimates of T_g generally show reasonable agreement. The maximum values of $\tan\delta$, a commonly published parameter, are only included for qualitative comparisons.

After the polymerized products were cooled with liquid nitrogen and then pulverized in a hammer mill, DSC runs were made at 20 °C min^{-1} under nitrogen using a Dupont 990 thermal analyser [12, 16, 17]. By the method of intersecting tangents, each T_g was determined.

Solid-state NMR measurements were performed on a Chemagnetics CMC200S spectrometer operating at 200 MHz for protons (^{1}H). Cross-polarization (CP) magic-angle-spinning (MAS) techniques were used to obtain high-resolution, solid-state ^{13}C NMR spectra of the specimens. Standard pulse sequences with carbon detection were used to measure the proton and carbon rotating-frame relaxation times $T_{1\rho}$ at radio-frequency field intensities around 50 kHz. These $T_{1\rho}$ were chosen because they are sensitive to both molecular motion and sample homogeneity, but in different ways [18]. Supplementary information regarding this methodology and a model are provided in Appendix A.

3. Results

From the characteristic changes in E', $\tan\delta$ and Δl for all of the plasticized PMMA samples (Table I), the values of T_g decreased as the plasticizer content increased. Similarly, a gradual depression of E' at 37 °C was observed as the proportion of DBP in PMMA increased (Table I).

DMA measurements were made on PMMA, and typical plots of $\log E'$, $\log E''$, and $\log \tan\delta$ versus temperature are shown in Fig. 1a. Fig. 1b represents a typical plot of Δl versus temperature for PMMA. Figs 2a and b represent the comparable dynamic behaviour of PMMA that has been plasticized with 15% v/v DBP over the same temperature range (− 150 to 170 °C).

The T_g data, as obtained from Δl versus T plots for all DBP plasticized compositions of PMMA, conformed to a rule-of-mixtures relation and gave a linear plot ($1/T_g$ versus volume fraction of PMMA) with a negative slope (Fig. 3 and Table I). A similar relationship was observed with reference to the data obtained from the DSC method (Fig. 4 and Table I).

Figs 5, 6 and 7 show characteristic changes in E', $\tan\delta$ and Δl, respectively, as a function of temperature for all plasticized compositions of PMMA.

Fig. 8 shows the influence of plasticizer content on $T_{1\rho}$ (Table I). The solid line corresponds to $R_m = 58.6$ Hz, $R_d = 1230$ Hz, and $R_d^0 = 0$ Hz, defined in Appendix A (cf. Equation A1). A non-zero value for the last parameter did improve the fit somewhat (cf. the dashed line, in which $R_m = 58.0$ Hz, $R_d = 1165$ Hz and $R_d^0 = 25.0$ Hz), but at this time the data do not justify a three-parameter fit.

TABLE I Glass-transition temperatures, T_g, storage moduli, E', and relaxation times, $T_{1\rho}$, of poly(methyl methacrylate) as a function of dibutyl phthalate (DBP) contents

Plasticizer Content (% v/v DBP)	T_g (°C)[a] From E'	From $\tan\delta$	From Δl	T_g (°C) From DSC	$E' \times 10^{-10}$ (N m^{-2})[b]	$T_{1\rho}$ (^{1}H) (ms)[c]
0	124	(141)	125	107	0.161	17.54
3	–	–	–	100	–	17.06
5	111	(131)	111	–	0.124	–
6	–	–	–	–	–	17.04
10	87	(109)	87	81	0.117	–
15	78	(100)	74	60	0.121	–
18	–	–	–	–	–	12.75
19	–	–	–	–	–	11.56
20	61	(89)	59	32	0.112	–
25	44	(64)	41	28	0.060	–
30	39	(60)	37	–	0.045	6.37
33	–	–	–	–	–	5.73

[a] Evaluated at 11 Hz.
[b] Evaluated at 37 °C and 11 Hz.
[c] Evaluated at 25 °C and 50 kHz.

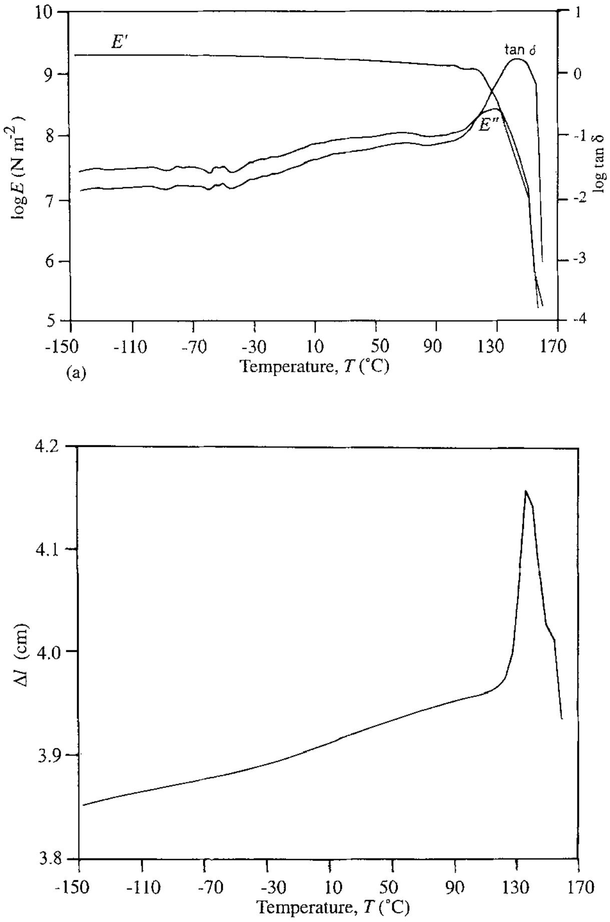

Figure 1 Representative plots of the dynamic mechanical properties for unmodified poly(methyl methacrylate) (PMMA): (a) storage modulus, E', loss modulus, E'' and loss tangent, tan δ, versus temperature, T; and (b) change in length, Δl versus T.

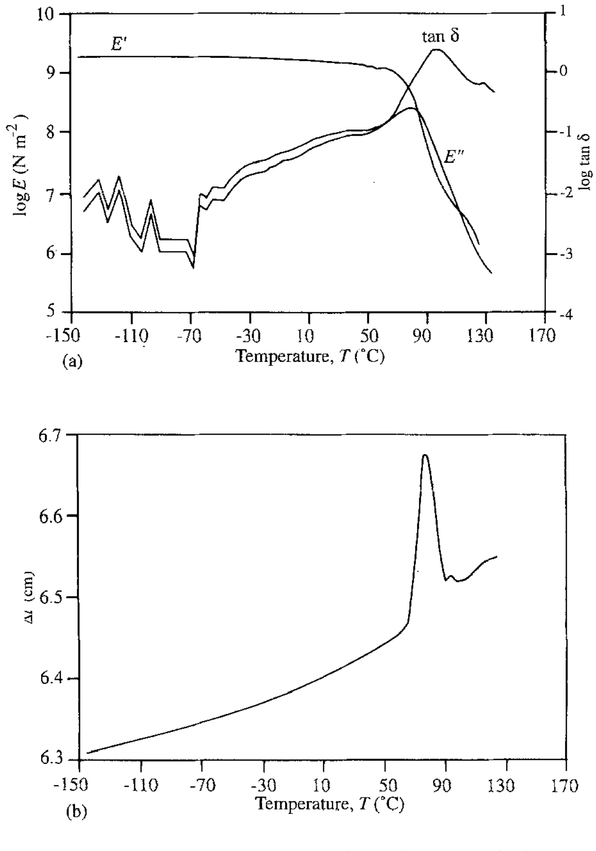

Figure 2 Representative plots of the dynamic mechanical properties for PMMA plasticized with 15% v/v dibutyl phthalate (DBP): (a) E', E'', and tan δ versus T; and (b), Δl versus T.

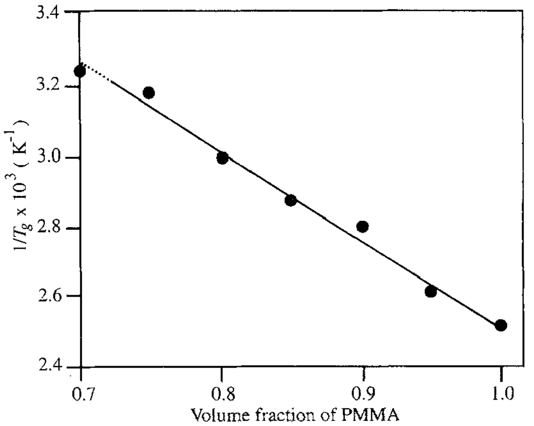

Figure 3 Conformation of the T_g data obtained from dynamic mechanical analyses (Table I to Equation 2 for the PMMA–DBP system.

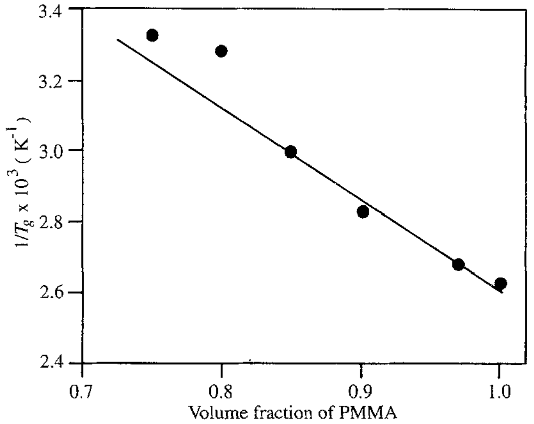

Figure 4 Conformation of the T_g data obtained from differential scanning calorimetry measurements (Table I) to Equation 2 for the PMMA–DBP system.

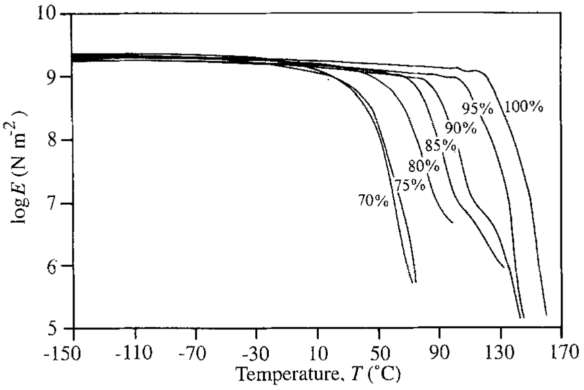

Figure 5 Summary of E' versus T plots for unplasticized PMMA and six plasticized PMMA compositions ranging from 5 to 30% v/v DBP. Note that in the two highest-plasticized specimens the antiplasticization effect occurs at $T < 25$ °C.

4. Discussion

DMA allows the determination of important properties – such as the dynamic Young's modulus via E', internal friction via tan δ, and thermal expansion via Δl – over a wide range of temperatures at selected frequencies. At T_g, there are characteristic changes in E', tan δ and Δl. Just below the T_g, the polymer is in a glassy (rigid) state in which chain segments are

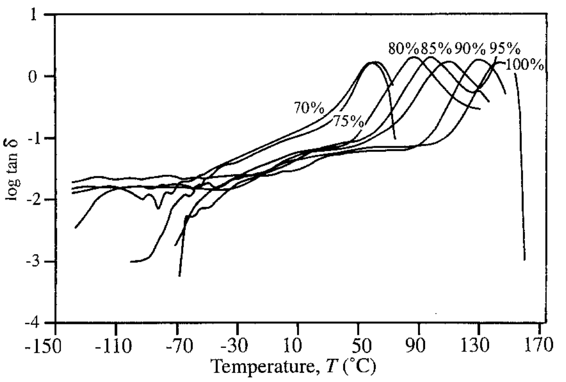

Figure 6 Summary of tan δ versus T plots for unplasticized PMMA and six plasticized PMMA compositions ranging from 5 to 30% v/v DBP. Note how the peak of the tan δ versus T plots tends to overestimate the true T_g values (cf. Table I).

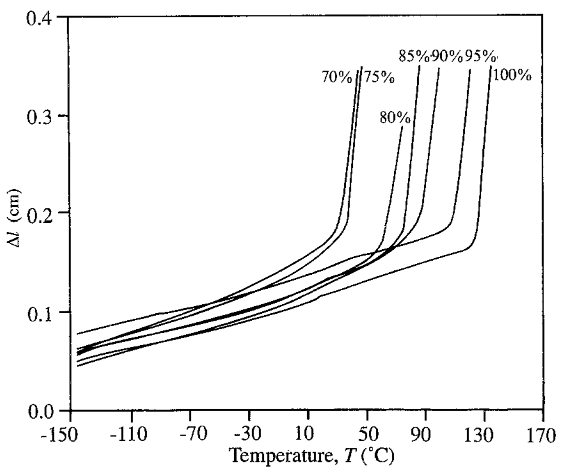

Figure 7 Summary of Δl versus T plots for unplasticized PMMA and six plasticized PMMA compositions ranging from 5 to 30% v/v DBP. To eliminate unnecessary clutter, note that the negative slopes of the curves at high temperatures were deleted (cf. Figs. 1b and 2b). Moreover, unlike Figs 1b and 2b, in which absolute values of Δl were given, these Δl values are relative to the initial value in the scan (e.g. 3.8 cm in Fig. 1b and 6.3 cm in Fig. 2b).

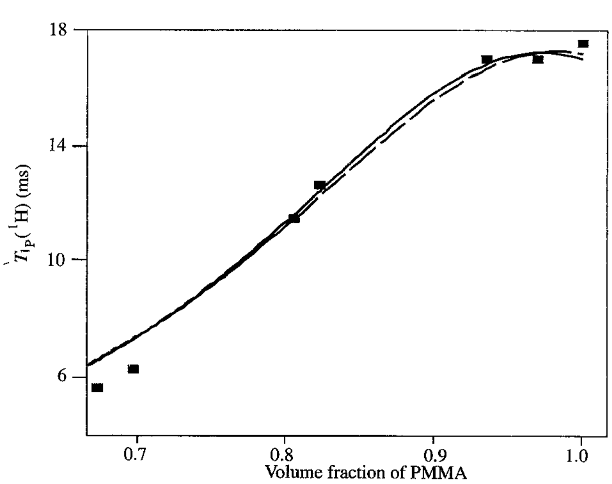

Figure 8 $T_{1\rho}$ (^{1}H) versus volume fraction of PMMA in a DBP plasticized system. The radiofrequency field intensity was 50 kHz at room temperature. The two curves correspond to Equation A1, with the specific parameters indicated in the text. The DBP concentrations were determined directly from the relative intensities of the DBP and polymer signals in the NMR spectra, since this procedure provided the most reliable sample concentrations [19].

frozen; whereas, some fifty degrees above the T_g, polymers are rubber-like. In this latter state, chain segments are free to move. The data obtained by the DMA technique (Fig. 3) and that obtained by the DSC technique (Fig. 4) conformed well to the general form of the rule of mixtures for an aggregate composite.

$$P^n = \alpha P_m^n + (1 - \alpha)P_d^n \qquad (1)$$

(the subscripts "m" and "d" are defined below) in which the property P and the exponent, n, are set equal to T_g and -1, respectively, such that

$$1/T_g = \alpha/T_{gm} + (1 - \alpha)/T_{gd} \qquad (2)$$

For the present work, α is the volume fraction of the polymer and $(1 - \alpha)$ is the volume fraction of the plasticizer. (Equation 2 corresponds to the traditional weight-fraction relation between T_g and co-polymer compositions [20] for the special case in which the specific gravities of the polymer and plasticizer are equal to unity. From calculations based on handbook values, the maximum error represents only a compositional difference of 28% v/v versus 30% v/v for the PMMA–DBP system.) In general, T_g for many polymer–plasticizer systems is a linear function of the volume fraction of the *matrix* or polymeric component (subscript "m") and their *dispersed* or plasticizer component (subscript "d"). From a plot of $1/T_g$ versus α (Fig. 3), the slope equalled -2.46×10^{-3} K^{-1}. This translated to a T_g for unplasticized PMMA of 133 °C, which is in general agreement with the experimental value of 125 °C (Table I), although it is somewhat greater than the value of T_g derived from the slope of the DSC data (113 °C, Fig. 4). The intercept of Fig. 3, 4.98×10^{-3} K^{-1}, gave a T_g of -72 °C for DBP. This T_g value is reasonable for a phthalate ester of this type [12, 21–23] and has been supported by the results obtained from the DSC measurements of Fig. 4 ($T_g = -81$ °C).

The influence of the plasticizer may be analysed in terms of the depression of T_g, E', and $T_{1\rho}$ (Table I and Figs 3–8).

The depression of T_g in all the plasticized compositions of PMMA (Table I, and Figs 3 and 4) has been interpreted as due to "the physical loosening of bonds" [24], i.e. to decreasing forces of attraction between polymer-chain segments. Consequently main-chain motion increases, resulting in a decrease in activation energy followed by a rapid increase in the diffusion coefficient, D, above T_g for water sorption of PMMA plasticized with DEP and DOP [16] as osmotic effects dominate absorption [25]. Parallel observations have also been made with reference to the water sorption of DBP-plasticized PMMA. In those experiments, a monotonic increase was observed in the values of D up to the T_g. Subsequently, D increased more markedly above the T_g [17]. Such an observation would be in agreement with the diffusion of water through a greater free volume which was caused by a plasticizer that had increased the main-chain motions of the polymer.

The second influence of the plasticizer is to affect the dynamic mechanical properties of the polymer (Figs

5–7), such as E'. Up to about 25% v/v of DBP, the E' of PMMA decreased monotonically, indicating a pronounced plasticization of PMMA by DBP at $T > 40\,^{\circ}\mathrm{C}$ (Fig. 5). Above about 25% v/v of DBP, however, the magnitudes of E' not only changed little but also reversed their relative positions at $T < 25\,^{\circ}\mathrm{C}$. This antiplasticization effect became apparent at $T < -25\,^{\circ}\mathrm{C}$ and has been explained by a loss of free volume and a subsequent suppression of chain motions [26]. The present observations agree with an earlier study in which the elastic modulus and tensile strength of PMMA exhibited maximum values at 26% v/v DBP [27]. Although the E'' peaks are not shown, the α-transition that is normally associated with the glass transition did inevitably merge at compositions of about 25% v/v with the invariant β-transition that is associated only with side-chain motion.

Ultimately, the thermal and mechanical properties measured previously mirror the $T_{1\rho}$'s determined by NMR. We have chosen two different $T_{1\rho}$'s which average molecular motion differently [18]. The $T_{1\rho}$ (^{1}H) relaxation is sensitive to macroscopic variations by the motion of the ^{1}H system averaged over a short distance; the $T_{1\rho}$ (^{13}C) relaxation reflects the motion of specific sites by monitoring individual ^{13}C spins. Furthermore in fundamentally homogeneous systems, $T_{1\rho}$ (^{1}H) tends to be dominated by the most efficient site of relaxation even if it is a minority site; $T_{1\rho}$ (^{13}C) reports the most common relaxation rate and deemphasizes minor sources of relaxation. When used together, these methodologies detect changes in molecular motion and motional inhomogeneity.

From a detailed comparison between pure PMMA and PMMA that had been polymerized with DBP, the spectra of the plasticized polymer show lines attributable to the plasticizer at 131 p.p.m. After an apparent induction period of about 5% v/v DBP (Fig. 8) [28], $T_{1\rho}$ (^{1}H) decreased from 17.5 to 12.8 ms upon incorporation of 18% v/v DBP (Table I). This striking change indicates that molecular motion has been considerably increased by the addition of plasticizer. More complete studies as a function of radiofrequency field indicate that both the frequency and amplitude of motion increase [29, 30]. Furthermore, the DBP line at 131 p.p.m. had a relaxation time of 10.6 ms, which is close enough to 11.0 ms to indicate intimate mixing of the DBP in the PMMA and that DBP is a source of relaxation and not just a participant in it.

When $T_{1\rho}$ (^{13}C) spectra were measured, the effect of the plasticizer was far less striking and proved deceptive, apparently indicating little change due to the addition of the plasticizer. In fact, the $T_{1\rho}$ (^{13}C) data obtained as a function of the radiofrequency field indicated an increase in chain motion. In this frequency regime, speeding up, by itself, increased $T_{1\rho}$ (^{13}C) as well as $T_{1\rho}$ (^{1}H). From the radiofrequency-field dependence of $T_{1\rho}$ (^{13}C), the increased amplitude of motion (which will decrease the value of $T_{1\rho}$) virtually cancelled the change due to the rate increase.

In summary, the $T_{1\rho}$ (^{13}C) results confirm a general loosening and separation of the polymer chains by the addition of DBP itself. On the other hand, the interpretation of $T_{1\rho}$ (^{1}H) must take the contribution of the DBP directly into account, since the relaxation of the protons in DBP are part of the total proton-relaxation picture.

5. Conclusions

1. From both dynamic mechanical measurements and DSC measurements, the glass-transition temperatures of poly(methyl methacrylate) (PMMA) plasticized with dibutyl phthalate (DBP) conformed to a simple, linear relation up to about 30% v/v DBP.

2. The plasticized compositions of PMMA (i.e. 25 and 30% v/v DBP) exhibited limited antiplasticization at temperatures below $-25\,^{\circ}\mathrm{C}$.

3. NMR relaxation measurements, which are sensitive to changes in molecular motion, indicated that pure PMMA *versus* PMMA plasticized with 18% v/v DBP exhibited an increase in the average chain motion, the frequency and the amplitude. Studies from 0 to 33% v/v DBP in PMMA showed that the DBP passes through an induction period prior to plasticization at about 5% v/v DBP.

4. The combination of dynamic mechanical measurements, DSC, and solid-state NMR measurements provides substantial indirect evidence that the depressions of the second-order transition, the elastic constants, and the relaxation times are caused by an increase in polymer main-chain motion via the physical loosening of secondary bonds between polymer chains.

Appendix A

The combination of cross-polarization, high-power proton decoupling, and magic-angle sample spinning makes it possible to obtain liquid-like, high-resolution, rare-spin (usually ^{13}C, but sometimes ^{16}N, ^{29}Si, ^{31}P, etc.) NMR spectra in organic solids. This technique is particularly well-suited to the study of polymers. Since NMR is non-destructive, a sequence of chemical or physical changes may be studied on the same specimen. Such experiments require the manipulation of both the abundant spin (^{1}H) and the rare spin (^{13}C) along the radiofrequency fields that are appropriate to each. These manipulations depend upon several rotating-frame relaxation times ($T_{1\rho}$), most notably $T_{1\rho}$ (^{1}H) and $T_{1\rho}$ (^{13}C), which are sensitive to the frequency and amplitude of the motion of the spin system being studied [18]. Frequencies in the range from a few kHz to a few hundred kHz are the most important in determining these $T_{1\rho}$; near room temperature, this frequency range reflects the motion of short segments of the polymer main chain, as well as side-chain motion. Anything that alters these motions may also alter one of the rotating-frame relaxation times.

The interpretation of $T_{1\rho}$ (^{1}H) must take the contribution of the DBP directly into account, since the relaxation of the protons in DBP are part of the total proton-relaxation picture. The dependence of $T_{1\rho}$ (^{1}H) on the volume-in-volume percentage of DBP measured at a radiofrequency field intensity of 50 kHz is shown in Fig. 8. In Fig. 8 the DBP concentrations were determined directly from the relative intensities of the DBP and polymer signals in the NMR spectra, since this procedure provided the most reliable sample concentration [19]. To fit the data in Fig. 8, the following equation is proposed,

$$1/T_{1_\rho}\,(^1\mathrm{H}) = X_m R_m + X_d(X_m R_d^0 + X_d R_d)\,, \quad \text{(A1)}$$

in which X_m and X_d represent the mole fraction of protons in the polymer or *matrix* phase and the plasticizer or *dispersed* phase, respectively. R_m represents the relaxation rate of the matrix protons; R_d^0 and R_d represent the dispersed relaxation rate at $X_d = 0$ and $X_d = 1$, respectively. This model assumes that communication between the two sources of relaxation is so efficient that only the weighted average rate is observed [18]. The plasticizer contribution to relaxation, $X_m R_d^0 + X_d R_d$, takes account of the changeover from rigid plasticizer molecules trapped between polymer chains (R_d^0) to liquid-like domains of plasticizer intermingled with the polymer (R_d).

Acknowledgements

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