Studies of Polymer Mobility in Composite Blends of Poly(vinyl butyral) and Alumina

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SYNOPSIS

Solid-state NMR and thermal analysis techniques were used to compare the mobility of poly(vinyl butyral) (PVB) in the presence and absence of both alumina filler particles and plasticizer. The relative mobility of main-chain and side-chain carbons increases in the presence of both plasticizer and alumina as seen from an increase in the average cross-polarization rates, $\langle T_{CH} \rangle$, and from a general decrease in the rotating frame spin-lattice relaxation rates, $^{C}T_{1\rho}$. Unlike the main-chain carbons, inversion recovery cross-polarization (IRCP) data on solution cast composites show that the side-chain methyl groups in neat PVB samples are best characterized by a monoexponential cross-polarization model. However, in the presence of alumina, a fraction of the methyl groups becomes less mobile as indicated by the biexponential IRCP behavior. Polymer phase mobility also increases below the critical pigment volume concentration (CPVC) as seen from decreasing transition temperatures using dynamic mechanical analysis (DMA) and differential scanning calorimetry (DSC). This is accompanied by an increase in the rigidity of a portion of the polymer phase above the CPVC as indicated by an increase in the apparent T_g, along with an increase in the mobility of another portion as indicated by the appearance of a low-temperature DMA transition. These trends are consistent with an increase in polymer chain packing heterogeneity in the presence of alumina. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

The macroscopic mechanical behavior of filled polymers is a complex function of filler properties, polymer properties, and coupling interactions between the filler particles and the polymer phase.[1] Formulation improvements are often based on empirical observations of macroscopic trends such as tensile strength, Young's modulus, and composite packing density. Although the properties of each individual component can be measured in isolation, it is difficult to separate the actual contribution of each phase to composite behavior. This is particularly a problem with the organic polymer phase since its molecular level behavior can be influenced by chemical or physical interactions at the inorganic particle interface.[2] Hence, there is a need for methods of analysis that allow for the direct observation of polymer phase behavior in a filled composite system.

Relaxation parameters from solid-state ^{13}C-NMR experiments have been frequently used to evaluate the relative mobility of polymer carbons in a variety of systems including composites.[3,4] Common experiments include T_1 and $T_{1\rho}$ spin-lattice relaxation, with each being sensitive to dipolar reorientation processes having frequency components in the MHz and kHz ranges, respectively.[5] Recently, the average cross-polarization (CP) rate between carbons and protons, $\langle T_{CH} \rangle$ as measured by inversion recovery cross-polarization (IRCP) experiments, has been used to develop correlations between main-chain motional behavior and macroscopic properties such as storage modulus.[6-8]

Given that T_{CH} is weighted by near static motional components,[9,10] it appears to be particularly sensitive to motions that are likely to influence the response of materials to mechanical deformations at low strain rates or at low-strain amplitudes during low-frequency dynamic experiments. Previous work on alumina-filled polystyrene systems has shown that IRCP can be used to determine the relative contribution of the polymer phase to the macro-

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scopic dynamic mechanical behavior of the composite.[11] Thus, IRCP should also be useful as a technique to compare the motional behavior of an isolated neat polymer to the motional behavior of the polymer phase as it exists in a highly filled polymer composite system. With this idea in mind, we have used IRCP in addition to $^{C}T_{1\rho}$ to evaluate the affect of plasticizer and alumina filler on the relaxation behavior of poly(vinyl butyral) (PVB) carbons. These results were then compared to trends in apparent transition behavior using differential scanning calorimetry (DSC) and (DMA) dynamic mechanical analysis techniques.

EXPERIMENTAL

PVB containing approximately 14% vinyl alcohol functionality (M_w = 100,000) was obtained as a commercial product known as Butvar from the Monsanto Chemical Co. The PVB was dissolved at a concentration of 20% by weight in a mixture of solvents from Fisher containing 55% toluene and 45% ethanol by weight. A similar solution containing 20% plasticized PVB by weight was prepared by mixing PVB with tributyl citrate (TBC) at a ratio of 75% to 25% by weight in the 55/45 toluene ethanol mixture, where the TBC was obtained as the commercial product Citroflex-4 from Morflex Chemical. Neat films of PVB and PVB/TBC were cast from these solutions and air-dried at 23°C with 50% relative humidity for at least 4 weeks prior to analysis. The same vehicle solutions were also mixed with Alcoa alumina (5 μm average particle diameter, 0.8 m²/g) to yield cast films containing 88% alumina and 12% organic polymer by weight. These films were also air-dried for at least 4 weeks prior to analysis by solid-state NMR.

Solid-state NMR experiments were run on a GE-300 instrument at 75 MHz for ^{13}C analysis with magic angle spinning at 3000 Hz using sealed Kel-F rotors. High-power proton decoupling was used with a proton 90° pulse of sufficient duration to provide an effective decoupling frequency of 53 kHz during data acquisition. All proton–carbon CP experiments were performed with a Hartmann–Hahn match contact time of 0.75 ms followed by either a $^{C}T_{1\rho}$ rotating frame spin-lattice relaxation pulse sequence[9] or by an IRCP sequence.[12] Signal averaging of 600 transients was used for neat films, whereas 2000 transients were required for adequate signal to noise in the films containing alumina with a recycle time of 5 s between transients in all cases.

$^{C}T_{1\rho}$ values were measured by taking the inverse slope of the natural log of integrated peak intensities vs. delay time where 18 delay times were used ranging from 0.1 to 35 ms. All the $^{C}T_{1\rho}$ experiments were adequately described by single exponentials with correlation coefficients of .98 or better. IRCP experiments were run with 20 inversion contact times ranging from 5 to 2000 μs. T_{CH} and $^{H}T_{1\rho}$ values were obtained by curve fitting the integrated peak intensities to monoexponential and biexponential models accounting for competitive $^{H}T_{1\rho}$ decay.[13] All analyses were performed on the main-chain butyral carbon at 102 ppm and on the side-chain methyl carbon at 15 ppm since these peaks provided the least amount of spectral overlap[14] and the best signal to noise of all carbons, particularly in the filled samples.

In separate tests, a vehicle solution of 20% PVB in 55/45 toluene/ethanol was mixed with alumina to yield cast films ranging from 0 to 93% alumina by weight. The bulk densities of cast films were calculated with measured dimensions and weights. The transition behavior of each sample was then analyzed with a Perkin-Elmer DSC-7 and a DMA-7.

DSC experiments were run with controlled cooling at 5°C/min to −20°C followed by controlled heating at 20°C/min to 120°C. The apparent glass transition temperatures were taken from the most pronounced inflection points of the relative heat capacity vs. temperature curves. DMA experiments were run at a fixed frequency of 1 Hz using a controlled-strain amplitude of 0.012% over a temperature range −20 to 60°C. DMA transition temperatures were taken from the apparent loss modulus maxima in each case.

RESULTS AND DISCUSSION

Solid-state ^{13}C-NMR spectra for the neat PVB film and the filled system are shown in Figure 1. The difference in resolution is due to the low polymer concentration in the filled system. Previous peak assignments for PVB have shown that the resonance at 102 ppm is the main-chain butyral ring carbon with no overlapping resonances due to tacticity. Similarly, the resonance at 15 ppm is assigned to the methyl group on the butyral side chain with no tacticity effects.[14] The unambiguous assignments of these carbons makes them useful for relaxation studies, particularly in the filled systems that show less resolution. Hence, the relaxation parameters for the 102 and 15 ppm carbons are given in Tables I and II, respectively.
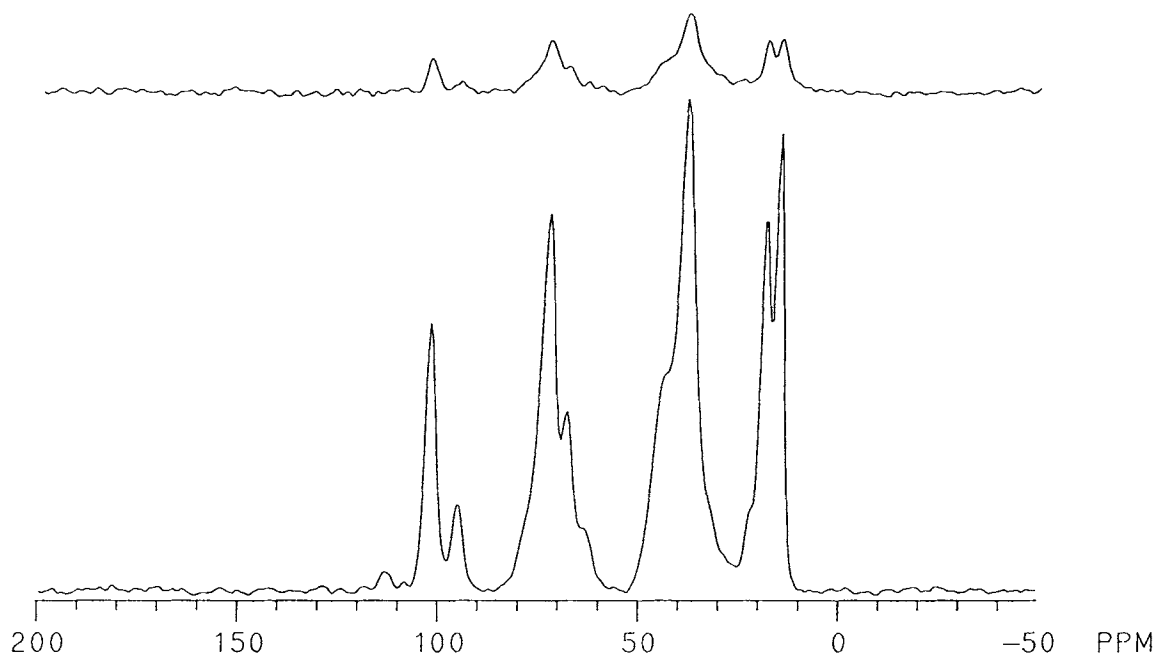
Figure 1 ^{13}C-CP/MAS-NMR spectra of (bottom) solution-cast neat PVB film and (top) PVB with 88% alumina.

Solid-state NMR Experiments on Neat Films: Effect of TBC

With the exception of the 15 ppm methyl carbon in both the neat PVB and neat PVB/TBC samples, all the IRCP data were best-fit to a biexponential CP model accounting for competitive $^{H}T_{1\rho}$ relaxation. Biexponential fitting leads to two CP time constants, T_{CHA} and T_{CHB}, as well as the fractional percentage of each cross-polarizing component, X and $1 - X$, respectively. These parameters can then be used to calculate the average CP rate, $\langle T_{CH} \rangle$.[6]

Multiple CP rates are often observed for main-chain polymer carbons since a variety of packing arrangements are available in the solid state even in predominantly amorphous polymers. This heterogeneity can be relatively static as in the case of semicrystalline polymers like polyethylene or polypropylene[12] or the heterogeneity can be more dynamic as in the case of polystyrene where local chain fluctuations in the solid state lead to multiple packing rearrangements.[9] The sensitivity of NMR relaxation parameters to these phenomena will depend on the motional frequency regime that influences the relaxation parameter, as well as the time scale of the NMR experiment.

The CP process typically occurs on the order of microseconds and scales with the spatial proximity of protons by a $1/r^6$ dependence. Hence, the time scale of the IRCP experiment is short compared to

Table I   Solid-state NMR Relaxation Parameters for PVB "Butyral Carbon" at 102 ppm in the Presence and Absence of Alumina and TBC

Sample	Best-fitting[a] IRCP Model	X	T_{CHA} (μs)	T_{CHB} (μs)	$\langle T_{CH} \rangle$ (μs)	$^{H}T_{1\rho}$ (ms)	$^{C}T_{1\rho}$ (ms)
PVB	2 (.99)	0.44	16	390	230	2.3	1.7
PVB/Al$_2$O$_3$	2 (.99)	0.39	17	600	370	4.6	0.9
PVB/TBC	2 (.99)	0.46	23	430	240	1.3	1.1
PVB/TBC/Al$_2$O$_3$	2 (.98)	0.40	30	760	470	2.6	1.1

[a] The best-fitting model is either a monoexponential or biexponential CP model accounting for competitive $^{H}T_{1\rho}$ decay. Correlation coefficient (r) for the best fit model is also given.

Table II Solid-state NMR Relaxation Parameters for PVB Methyl Carbon at 15 ppm in the Presence and Absence of Alumina and TBC

Sample	Best-fitting[a] IRCP Model	X	T_{CHA} (μs)	T_{CHB} (μs)	$\langle T_{CH} \rangle$ (μs)	$^{H}T_{1\rho}$ (ms)	$^{C}T_{1\rho}$ (ms)
PVB	1 (.99)	—	420	—	420	4.20	5.2
PVB/Al$_2$O$_3$	2 (.98)	0.22	16	940	740	5.50	3.1
PVB/TBC	1 (.99)	—	610	—	610	0.960	3.1
PVB/TBC/Al$_2$O$_3$	2 (.99)	0.16	24	900	760	2.40	3.0

[a] See footnote a to Table I.

the time scale for long-range Brownian-type diffusion processes that occur in the glassy state of a solid polymer. However, despite the short time scale of the experiment, the CP rate is sensitive to near static components of molecular motion that are likely to be associated with long-range cooperative motional processes.[9]

The counteractive influence of the experimental time scale and of the motional frequency dependence increases the complexity of the CP process in polymers. Thus, it is common to observe biexponential CP rates for motionally restricted carbons like those located on the main chain of a polymer. In the case of PVB, the biexponential behavior of the 102 ppm carbon has been attributed to a static morphology of "rigid" and "mobile" environments.[13] Conversely, the less restricted motional behavior of a side-chain methyl group can lead to a homogeneous CP rate as we have observed here for the PVB methyl carbon.

The near static frequency dependence of the CP rate has made it possible to correlate the average $\langle T_{CH} \rangle$ for main-chain carbons with macroscopic mechanical properties such as dynamic storage and loss moduli.[7] In general, the shorter CP rates are indicative of restricted motion, whereas longer CP rates are indicative of less restricted motional behavior. This also makes the CP process sensitive to the effects of plasticization and antiplasticization.[10] Thus, trends in CP rates are likely to correlate with macroscopic trends that are influenced by long-range and, hence, near static motional processes.

The plasticization effect of TBC in this study leads to longer CP rates for both the backbone and side-chain carbons in PVB. This is paralleled by a decrease in $^{C}T_{1\rho}$, which indicates that the amplitude of kHz motional processes is also increased in the presence of TBC.[9] The apparent $^{H}T_{1\rho}$ values also decrease in the presence of TBC plasticizer. However, since $^{H}T_{1\rho}$ is influenced by both proton spin diffusion and kHz motion,[15] it is impossible to at-

tribute this trend to motion alone. Nevertheless, the change in $^{H}T_{1\rho}$ does indicate that the proton dipolar environment has been altered in the presence of TBC.

Solid-state NMR Experiments on Neat Films: Effect of Alumina

The addition of alumina to the PVB films has a pronounced effect on the relaxation behavior of both the main-chain and side-chain carbons. The presence of alumina leads to an increase in backbone mobility as can be seen from the increase in T_{CH} values for the 102 ppm carbon either with or without TBC plasticizer. Although the addition of alumina does not significantly affect the $^{C}T_{1\rho}$ for the plasticized sample, the $^{C}T_{1\rho}$ values decrease significantly when alumina is added to the neat PVB, which is indicative of less restricted motion in the kHz range.

The addition of alumina also leads to biexponential CP behavior for the PVB methyl carbons. Figure 2 shows the fit of a monoexponential CP model to the methyl carbon IRCP data in the neat film. The monoexponential model provides a good fit in this case with a correlation coefficient of $r = .99$. However, an attempt to use the monoexponential model for the methyl carbon in the presence of alumina leads to a poor fit with a correlation coefficient of $r = .86$ as shown in Figure 3. Thus, in the presence of alumina, the methyl carbon is best described by a biexponential model with $r = .99$ as shown in Table II. This indicates that the methyl carbon exists in two motional environments (on the time scale of the IRCP experiment) in the presence of alumina. One of the environments is more motionally restricted as indicated by a short T_{CHA}, and the other is less restricted as indicated by the longer T_{CHB}.

Since the methyl T_{CHB} values are longer than the T_{CH} values that were observed in the neat samples, it appears that the methyl group mobility in the en-
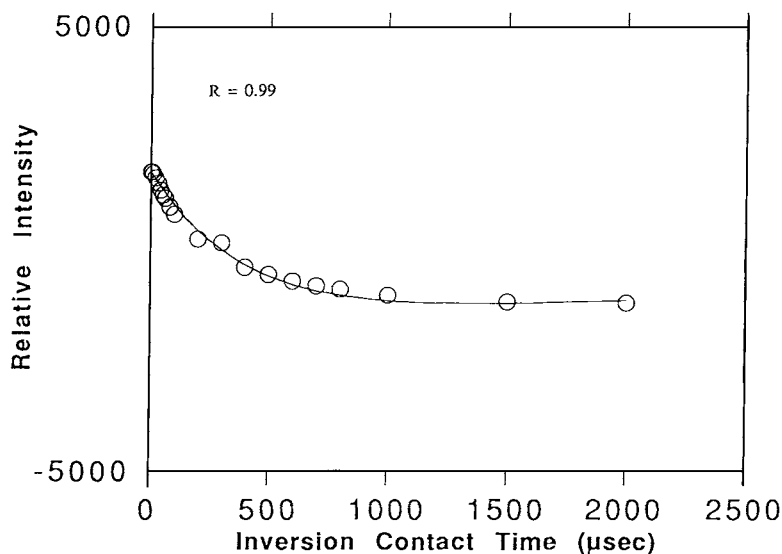
Figure 2   PVB neat film monoexponential model fit of methyl carbon IRCP.

vironment associated with T_{CHB} is less restricted than in the neat films. Thus, the presence of alumina leads to an environment with enhanced methyl group motion in addition to a second environment with more restricted motion. The methyl group also exhibits enhanced kHz motion in the presence of alumina, as can be seen from a decrease in $^{C}T_{1\rho}$, particularly in the absence of TBC. The trend of increased methyl carbon mobility in the presence of alumina is also parallel to main-chain carbon behavior.

The addition of alumina also changes the proton dipolar environment as can be seen from changes

in $^{H}T_{1\rho}$ for both the methyl- and main-chain carbons. It is generally difficult to separate spin-lattice from spin-diffusion effects. However, in these cases, $^{H}T_{1\rho}$ increases in the presence of alumina, while $^{C}T_{1\rho}$ either decreases as in the case of the neat PVB or remains unchanged as in the case of PVB with TBC. Thus, the spin-lattice motional contribution to $^{H}T_{1\rho}$ is small compared to the contribution from spin diffusion.

The rate of spin diffusion among protons in a polymer is a function of both motion and proton internuclear distances.[16] Thus, spin diffusion can be sensitive to spatial packing arrangements as well as
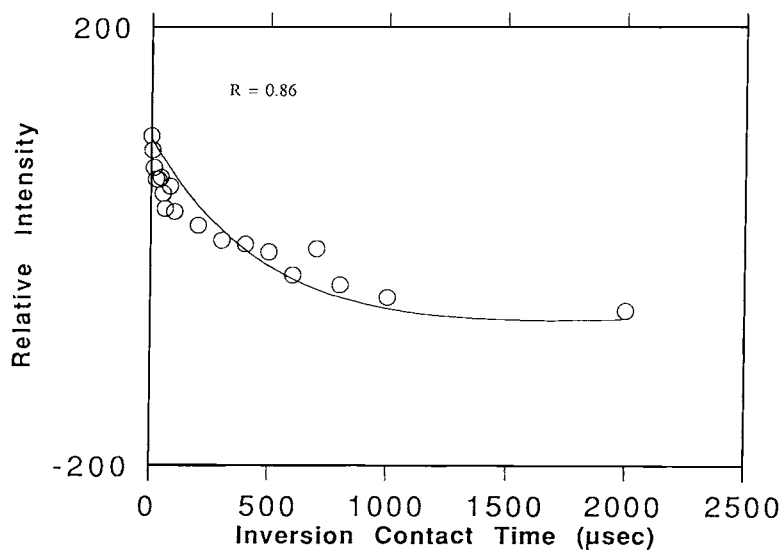

Figure 3   PVB/alumina monoexponential model fit of methyl carbon IRCP.

to static components of molecular motion. The high abundance of protons in vinyl polymers often leads to efficient proton spin diffusion (energy conserving spin flip-flop processes) over large spatial domains between chains and among neighboring monomer units within the time scale of an NMR relaxation measurement. This often leads to an averaging of the spin-diffusion rate for protons independent of their positions on the main chain. However, motion will tend to decrease the efficiency of proton dipolar coupling, leading to a lesser degree of spin averaging and to slower spin-diffusion rates. Thus, the increase in $^H T_{1\rho}$ values in the presence of alumina is most likely related to a change in the local dipolar environment either as a result of different chain packing arrangements or as a result of changes in the degree of near static motion as previously reflected by the increase in T_{CH} values.

Effect of Alumina on Apparent T_g Behavior

The major transition temperatures as a function of alumina-loading levels are displayed in Figure 4. Only one major transition is observed by both DMA and DSC measurements in solution cast composites with less than 72% alumina by weight. Prior studies of neat and plasticized PVB samples have shown the presence of multiple transitions.[10] The absence of these transitions in this study may be a result of both the limited temperature range of measurements and differences in morphology between solution-cast and extrusion-processed films. However, additional transitions do appear at about 25 and 75°C in DMA scans of composites with greater than 72% alumina by weight.
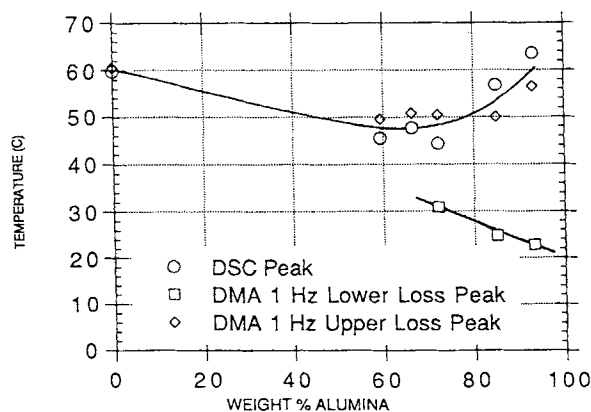

Figure 4 Effect of alumina-filler concentration on thermal and mechanical transition temperatures as determined by DSC and DMA measurements.

The increased polymer phase mobility in the presence of alumina as indicated by solid-state NMR measurements is paralleled by a general decrease in the apparent glass transition temperature up to a critical concentration of about 72% alumina by weight. Beyond this level, the apparent T_g seems to increase while a second lower temperature transition appears. These results collectively show that the polymer component becomes increasingly mobile up to a level of about 72% alumina. Beyond this level, a portion of the polymer phase continues to show enhanced mobility, and a second portion shows increased rigidity.

The density of the composites as shown in Figure 5 increases until a critical concentration is reached at about 72% alumina. This is followed by a decrease in density, suggesting that the critical pigment volume concentration (CPVC) occurs at an alumina loading level of approximately 72%.[17] Beyond the CPVC, the volume of polymer is not adequate to fill the interstitial spaces that separate the particles. Thus, the concentration of voids tends to increase, which results in a lower composite density.[17]

Given that multiple transitions are observed above the CPVC, it appears that the introduction of macroscopic void volume has an effect on polymer phase mobility. Since the NMR data shows that the polymer backbone has enhanced mobility in the presence of 88% alumina, and since DMA shows the existence of a low-temperature transition in the presence of alumina at both the 85 and 93% levels, it follows that a portion of the polymer phase has a higher fraction of free volume in the presence of alumina. Even below the CPVC, the apparent glass transition shifts to lower temperatures, which indicates that the free-volume fraction in the bulk polymer phase increases as a function of filler concentration.

A portion of the polymer phase also appears to have less free volume above the CPVC, as indicated by the increase in the apparent T_g from DSC and by the increase in the higher-temperature DMA transition. The NMR results for the polymer backbone carbons do not correlate with this trend. However, the relaxation behavior of the methyl group on the PVB side chain confirms the appearance of a motionally restricted environment in addition to a more mobile environment above the CPVC.

CONCLUSIONS

It is generally accepted that a certain portion of the polymer phase may be motionally restricted as a re-
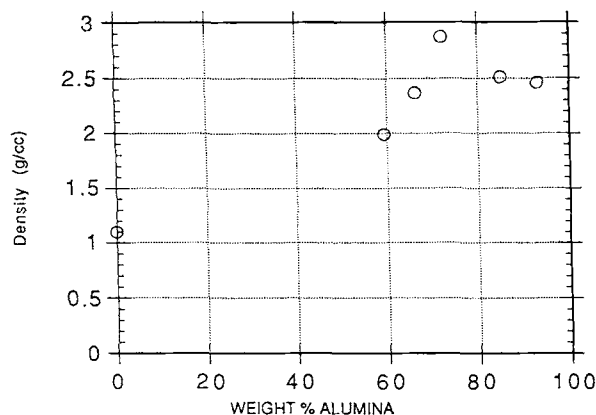
Figure 5   Effect of alumina-filler level on bulk composite density.

sult of polymer–particle surface interactions and that this can lead to a general increase in the glass transition temperature with increasing filler content.[2,4] On the other hand, the motional freedom of the nonadsorbed portion of the polymer phase has been observed to increase in the presence of filler,[4,17,18,19] particularly above the CPVC. Thus, it appears that a filler can influence polymer chain packing arrangements at locations beyond the particle–polymer interface.

Our DMA and DSC results on PVB systems filled with alumina show that polymer phase mobility can increase both below and above the CPVC. This implies that restricted segmental mobility (accompanied by the extended conformation of chains) that occurs at the polymer–particle interface[19] seems to promote loose chain packing in the bulk polymer phase, hence, resulting in less restricted mobility in the bulk polymer phase both below and above the CPVC. In addition, the introduction of void volume above the CPVC can lead to additional free volume and, hence, to an even greater enhancement in molecular mobility.[19]

In this study, the change in dipolar and, hence, polymer packing arrangements above the CPVC is supported by a change in spin diffusion rates as seen from apparent $^{H}T_{1\rho}$ measurements with solid-state NMR. A subsequent increase in molecular mobility is confirmed by an increase in the average CP rates for both the polymer backbone and the side-chain

methyl carbons. Finally, the biexponential IRCP behavior of methyl carbons in the presence of alumina provides further evidence for the increase in polymer chain packing heterogeneity.

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