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^{13}C Solid State NMR Study on the Dynamics of the Poly(vinyl butylal) with Various Water Contents

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Abstract : Physical properties of PVB [Poly(vinyl butyral)] polymer are strongly correlated with water contents in the polymer. Thus dynamics of PVB containing 10~50 (w/w) % of water were studied by ^{13}C CP/MAS/DD over the temperature range 293K – 348K. From the peak area, line width, chemical shift, and relaxation times (T_1, $T_{1\rho}$) measured at 9.4 T, it was deduced that water facilitates molecular dynamics of the PVB molecules overall including conformational exchange of the racemic and meso butyaldehyde rings in the PVB. However, the influence of water was not linear to the amount of water in the PVB samples. It is suggested that water up to 30 w/w % of the sample is closely bound to the PVB polymer and water relatively free from the PVB polymer starts to appear when water is added more than 30 w/w %.

INTRODUCTION

Glassy PVB [Poly(vinyl butyral)] polymer has been extensively used for sound and UV controlling glasses as well as safety glass due to greatly enhanced external impact absorption and excellent sound attenuation and ultraviolet filtering performance of the glasses interlayered with PVB. These macroscopic physical properties of PVB polymer are known to be intimately related to the polymer molecular dynamics, which is strongly influenced by water molecules in the polymer. Thus not only the main and the side chains' motional behavior[1-4] of synthetic polymers but also the motions and structural change of proteins[5] or the oxygen transporting through nylon-6 film[6-7] are affected by the waters in the substances. The water in a polymer can play a role of a plasticizer or antiplasticizer depending on the temperature and its concentration.[8-11] Plasticizer usually lowers the glass

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transition temperature, reduces the relaxation time, and increases the microscopic chain mobility. Visco-elastic properties of the polymer is also strongly controlled by a plasticizer. Depending upon the concentration of gas in a polymer, the gas molecules also can act as a plasticizer or an antiplasticizer, governing the physical properties of a polymer. For example, the main chain motion of the PVC is changed by the interaction of CO_2 and the polymer.[10,11]

However, the molecular level mechanism how the macroscopic polymer properties below T_g are influenced by the small molecule such as water is not well understood. The elucidation of the interrelationship between the molecular structure and dynamics of the polymer and the macroscopic properties such as mechanical properties below T_g is essential to understand the nature of the glassy polymer. Not only line widths but also relaxation parameters such as the ^{1}H and ^{13}C spin-lattice and spin-spin relaxation times (T_1, T_2) and the ^{1}H and ^{13}C rotating frame relaxation times ($T_{1\rho}$) can provide rich information on the molecular dynamics of a polymer. All the carbon-13 relaxation study has preponderance over the proton relaxation study because the fast spin diffusion among protons usually makes it difficult to interpret the proton relaxation data uniquely. Since Schaefer et al. have used ^{13}C relaxation measurements to probe polymer molecular dynamics for about two decade, many progresses in the better understanding of the physical properties of polymer molecules have been made.[12,13]

In this work the solid state CP/MAS/DD ^{13}C NMR technique yielding high resolution spectra is utilized to investigate the dynamics of each carbon in the PVB molecule below the T_g as well as the role of the water molecule in the polymer. A line width and a spin-lattice relaxation in a rotating frame, which are sensitive to the molecular motion, in addition to a chemical shift have been detected over the temperature range 298 ~ 353K.

EXPERIMENTAL

PVB(poly vinyl butyral) samples containing 10, 20, 30, 40, 50 w/w % water were provided by the polymer research center in the oriental chemical industry. ^{13}C CP/MAS/DD NMR spectra were acquired with a Larmor frequency of 105.8MHz on a Bruker DSX-400 NMR spectrometer with 4.5kHz spinning rate over the temperature range 298K – 353K. The contact time of 1 ms is employed under Hartman-Hahn condition with H_1 field strength of 50kHz. The chemical shift of ^{13}C was referenced to the left (down field shifted) peak of 38.3 ppm from the two peaks of the external adamantane sample. All relaxation (T_1 and $T_{1\rho}$) measurement pulse sequences were preceded by the CP in order to increase the sensitivity, and relaxations were determined over the temperature range 298 ~ 343K. The ~~inversion recovery pulse sequence of *delay-CP-π/2-τ-π/2* is used to measure the T_1 of each~~ carbon–13 with π/2 pulse = 5 μs. Rotating frame relaxation times of each carbon were obtained with spin lock field strength of 50 kHz.

RESULTS AND DISCUSSION

^{13}C CP/MAS/DD NMR Study

Fig. 1 shows the representative CP/MAS/DD carbon-13 spectra of PVB with various water contents at 298K. Peak deconvolution is needed to determine the precise peak positions and peak areas. The line width, peak area, and resonance frequency of the polymer with 10 w/w % water is representatively presented in Table 1. The line width and

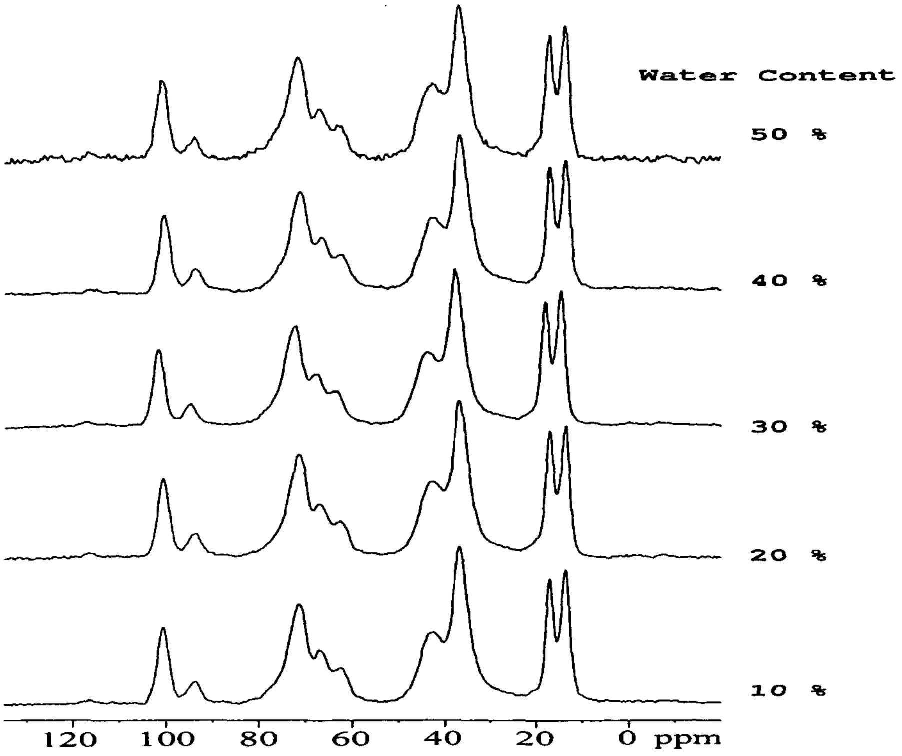

Fig. 1. Representative ^{13}C CP/MAS/DD spectra of PVB with various water contents in w/w % at 298 K.

Table 1. Resonance position (δ(ppm)), line width ($\Delta\nu_{obs}$), and peak area of the PVB with 10 w/w % water at various temperatures.

Temp (K)	298	308	318	328	338	343
δ(ppm)	100.6	100.6	100.6	100.7	100.6	100.6
$\Delta\nu_{obs}$	2.3	2.2	2.1	2.1	2.8	3.5
Area	6.7	6.3	5.4	4.0	2.1	3.2
δ(ppm)	93.7	93.7	93.9	94.0	94.2	94.1
$\Delta\nu_{obs}$	2.0	1.9	1.9	2.1	2.9	4.6
Area	1.4	1.4	1.2	1.1	0.6	1.2
δ(ppm)	71.6	71.6	71.8	72.1	72.2	72.5
$\Delta\nu_{obs}$	4.6	4.5	4.8	5.1	5.4	6.7
Area	15.4	14.4	12.7	9.5	4.5	7.3
δ(ppm)	66.4	66.4	66.5	66.7	65.7	67.5
$\Delta\nu_{obs}$	3.0	3.2	3.2	3.8	4.9	4.3
Area	3.5	3.8	3.1	2.6	3.6	1.3
δ(ppm)	62.4	62.4	62.7	63.2	63.8	64.3
$\Delta\nu_{obs}$	2.7	2.6	3.0	3.6	6.1	6.6
Area	2.5	2.3	2.0	1.7	0.1	3.9
δ(ppm)	43.1	43.1	43.1	43.1	43.1	43.6
$\Delta\nu_{obs}$	4.3	4.4	4.6	4.8	5.3	6.5
Area	9.0	9.0	8.0	5.9	2.1	3.3
δ(ppm)	36.6	36.6	36.7	36.6	36.6	36.6
$\Delta\nu_{obs}$	4.3	4.2	4.2	4.7	7.4	8.6
Area	21.7	20.5	16.7	11.9	7.8	11.5
δ(ppm)	17.0	17.0	17.0	16.9	16.8	16.8
$\Delta\nu_{obs}$	1.9	1.8	1.9	2.2	2.8	3.1
Area	7.6	7.3	6.4	5.2	3.4	6.1
δ(ppm)	13.6	13.6	13.6	13.6	13.5	13.5
$\Delta\nu_{obs}$	2.0	1.9	1.4	1.0	0.9	1.0
Area	9.0	8.3	6.7	5.3	4.2	7.2

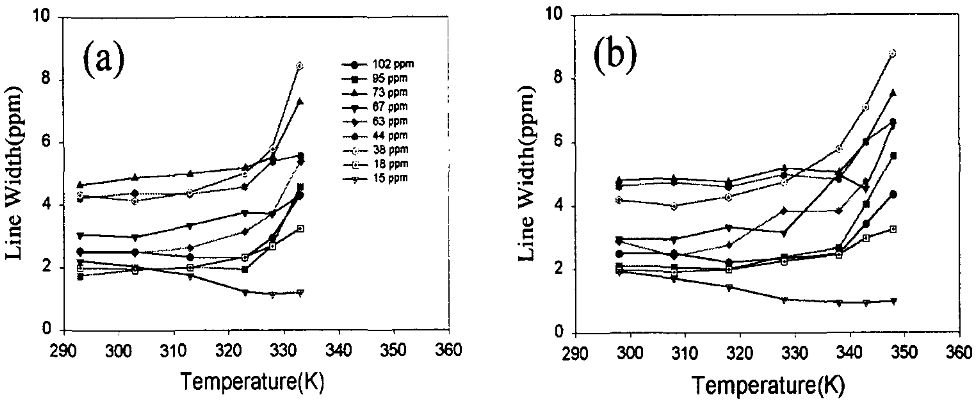

Fig. 2. Temperature dependence of the line widths of PVB polymers with 50 and 30 w/w % water.

peak area of PVB polymers with 30 and 50 w/w % water are plotted in Figs. 2 and 3, respectively. The increased line widths at higher temperature except for the methyl carbon peaks were observed in Fig. 2, which clearly indicates the most carbons except methyl carbon have modulation of the ^{13}C-^{1}H dipolar coupling in proton H_1 field frequency region. On the other hand, the molecular dynamics of the methyl carbon is much faster than the other carbons. The temperature at which the line widths of non-methyl carbons start to increase was highest for the sample with 30 w/w % water.

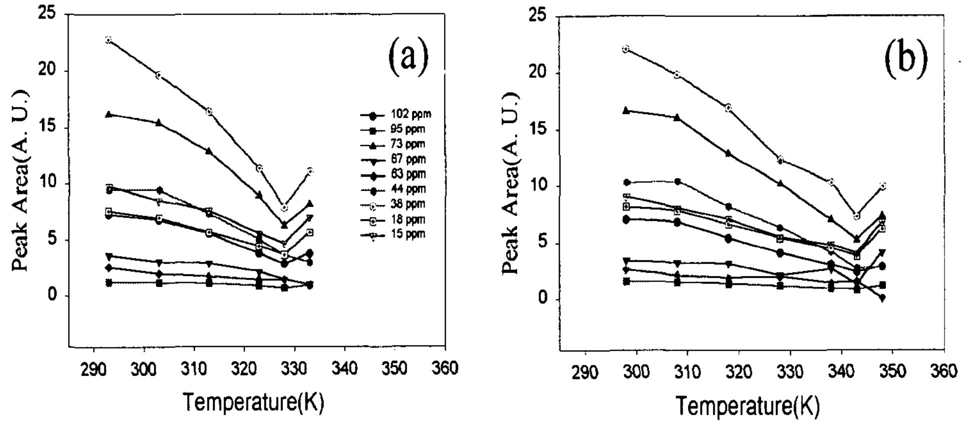

Fig. 3. Temperature dependence of the peak areas of the PVB with (a) 50 w/w % and (b) 30 w/w % water.

From the peak area data, it is noticed that the racemic isomer (peaks near 73 and 102 ppm) of PVB seems to dominate over the meso isomer (peaks near 67 and 95 ppm) in the sample. In general, the peak area decreases and begins to increase again as temperature is elevated but the temperature of the minimum peak area varies with the water content in the sample (Fig. 3). Among all samples, the PVB with 30 w/w % has the highest temperature for the minimum peak area.

The resonance frequency of each carbon in the PVB samples with different water contents was also compared and noticeable resonance frequency downfield shifts of the PVB with 30 w/w % water were detected at 298K (Fig. 4(a)). As temperature increases, the downfield shifts of resonance frequencies become relatively larger and the overall trends is complicated as shown in Fig. 4(b). The downfield shifts could be from hydrogen bonding between water and the hydroxyl and ester groups in the PVB, and from the change of the average conformation of each carbon due to different molecular dynamics in a given condition. Proton exchange between free water relatively remote from the PVB and water

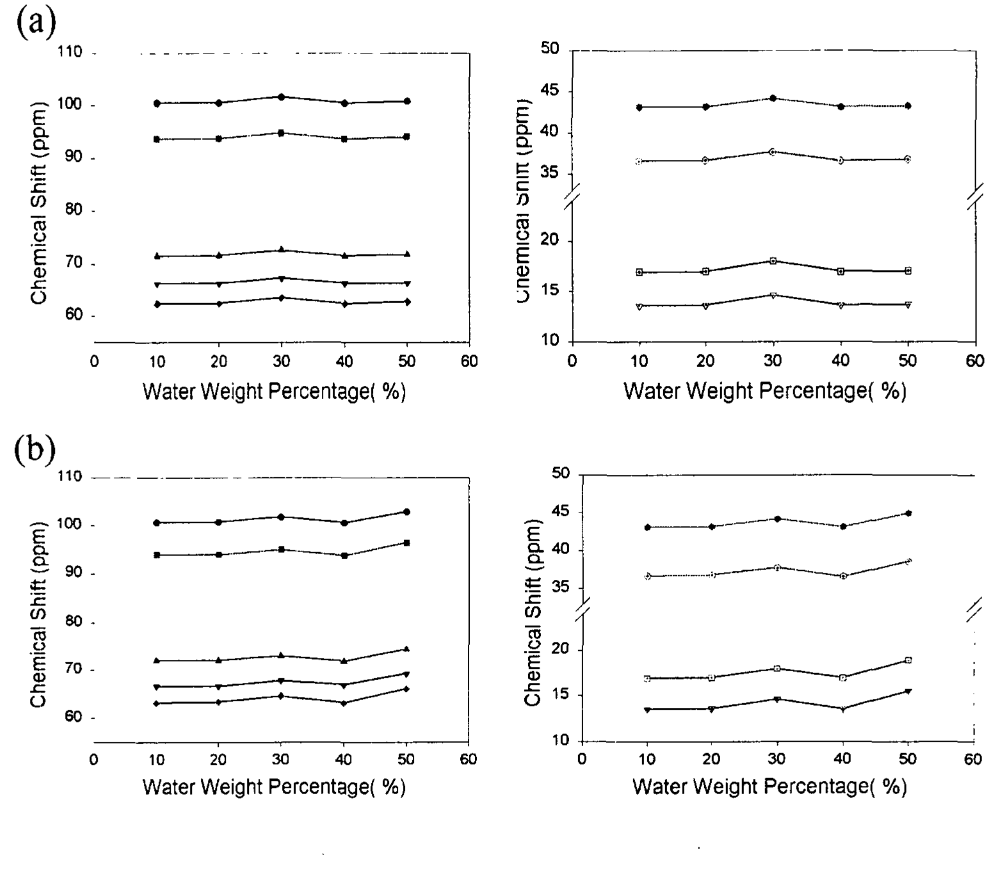

Fig. 4. Resonance line positions of PVB as a function of the water contents (a) at 298K and (b) at 328K

strongly bound to the PVB as well as between water and the PVB could affect the resonance frequency shifts. Dynamics variation of water molecules could influence the resonance frequency shifts also by changing the local electronic environments of each carbon.

^{13}*C Relaxation Study*

The local chain dynamics of the PVB with various water contents are monitored also by $T_{1\rho}$ and T_1 of ^{13}C. The T_1 and $T_{1\rho}$ at 50 kHz H_1 field of the PVB with 50 w/w % water are representatively presented in Table 2 and $T_{1\rho}$ data of the samples with different water percentages are plotted versus temperature in Fig. 5. The temperature dependence of the $T_{1\rho}$ illustrates the molecular correlation time of each carbon is mostly in the $\varpi_1\tau_c > 1$ region in the temperatures investigated. $T_{1\rho}$s of some carbons have minima in Fig. 5, while other carbons do not seem to reach minima yet. Thus, it can be deduced that the correlation time of the carbons with the $T_{1\rho}$ minima is approximately less than ~ μs at higher temperature than the $T_{1\rho}$ minimum temperatures, while those of the other carbons in the polymer fall into much longer than ~ μs.

But the T_1 data of the same sample in Table 2 do not illustrate any T_1 minimum over the same temperature range even for the methyl carbon. The T_1s of the given PVB sample are significantly longer than the $T_{1\rho}$s, which means that the local motion of polymer and/or the dynamics of water molecules in the sample is not fast enough to cause the T_1 relaxation effectively.[14,15] The $T_{1\rho}$ data of all the carbons of ploy(butyral-*co*-vinyl-alcohol) were reported to depend on H_1 field from 37kHz to 60kHz.[12] However, the $T_{1\rho}$s of fully plasticized ploy(butyral-*co*-vinyl-alcohol) by dihexyl adipate were much shorter than those of the polymer without dihexyl adipate and remained almost independent of the H_1 field.[12] This means the plasticizer, lowering the glass transition temperature of polymer and reducing its modulus, has a great impact on the local motion of the ploy(butyral-*co*-vinyl-alcohol). As a result, $T_{1\rho}$s were shortened enough to near the extreme narrowing region where $T_{1\rho}$s are independent of H_1 field.[16]

Fig. 5 denotes that the $T_{1\rho}$s of the PVB with 10 w/w % water at 300 K are much longer than those of the PVB samples with 30 w/w % water but the $T_{1\rho}$ variation of the PVB samples with 30 or more w/w % water is moderately governed by the water content. Much efficient relaxation of all carbons in the PVB with water indicates that water molecules help not only the side chains but also the main chains move faster. However, the molecular motion did not reach the extreme narrowing condition, implying that the water molecules play a role as a very weak plasticizer.

The conformational interconversion of the backbone chain in the many pendant polymers have been detected.[17-18] In Table 2, the relative integral ratio of the meso to the

Table 2. $T_{1\rho}$ and T_1 of each carbon in the PVB with 50 w/w % water at various temperatures.

Temp (K)	298	308	318	328	338	343
δ(ppm)	102.7	102.9	102.8	102.9	102.9	102.9
$T_{1\rho}$(ms)	26.9	21.8	10.1	3.4	2.4	1.7
T_1 (s)	-	21.9	19.6	15.4	14.4	-
δ(ppm)	95.8	95.9	95.9	96.2	96.5	96.6
$T_{1\rho}$(ms)	30.1	19.5	8.8	2.6	0.8	0.7
T_1 (s)	-	23.7	19.1	15.4	14.4	-
δ(ppm)	73.7	73.8	73.9	74.2	74.4	74.4
$T_{1\rho}$(ms)	20.3	15.4	7.6	2.7	1.5	1.0
T_1 (s)	-	25.8	18.7	18.5	15.9	
δ(ppm)	68.6	68.5	68.4	68.8	69.2	69.7
$T_{1\rho}$(ms)	15.5	11.1	5.5	1.8	-	-
T_1 (s)	-	13.8	10.2	6.0	-	-
δ(ppm)	64.5	64.5	64.8	65.7	66.2	66.5
$T_{1\rho}$(ms)	18.1	15.5	3.1	1.6	-	0.3
T_1 (s)	-	23.7	-	9.4	7.9	-
δ(ppm)	45.0	45.1	45.2	45.0	44.9	45.4
$T_{1\rho}$(ms)	6.7	5.2	3.3	1.5	1.0	0.5
T_1 (s)	-	15.6	8.4	10.3	9.5	
δ(ppm)	38.5	38.6	38.6	38.6	38.5	38.7
$T_{1\rho}$(ms)	8.6	6.7	3.5	1.7	1.0	0.6
T_1 (s)	-	16.3	12.4	8.4	7.9	5.1
δ(ppm)	18.9	19.0	18.9	18.8	18.9	18.8
$T_{1\rho}$(ms)	8.9	6.9	3.7	1.7	1.3	1.1
T_1 (s)	-	8.9	6.1	6.6	3.1	2.3
δ(ppm)	15.5	15.5	15.5	15.5	15.5	15.5
$T_{1\rho}$(ms)	46.3	37.5	20.0	9.2	8.7	11.5
T_1 (s)	-	12.5	13.3	10.6	8.3	4.5

racemic carbon peaks increases at higher temperature, which may mean the interconversion of the racemic and meso rings of the PVB. Higher temperature and sufficient water amount are expected to facilitate conformational exchange in general. The ring conversion observed also indicates that water in the PVB enables the main chain to be more motional.

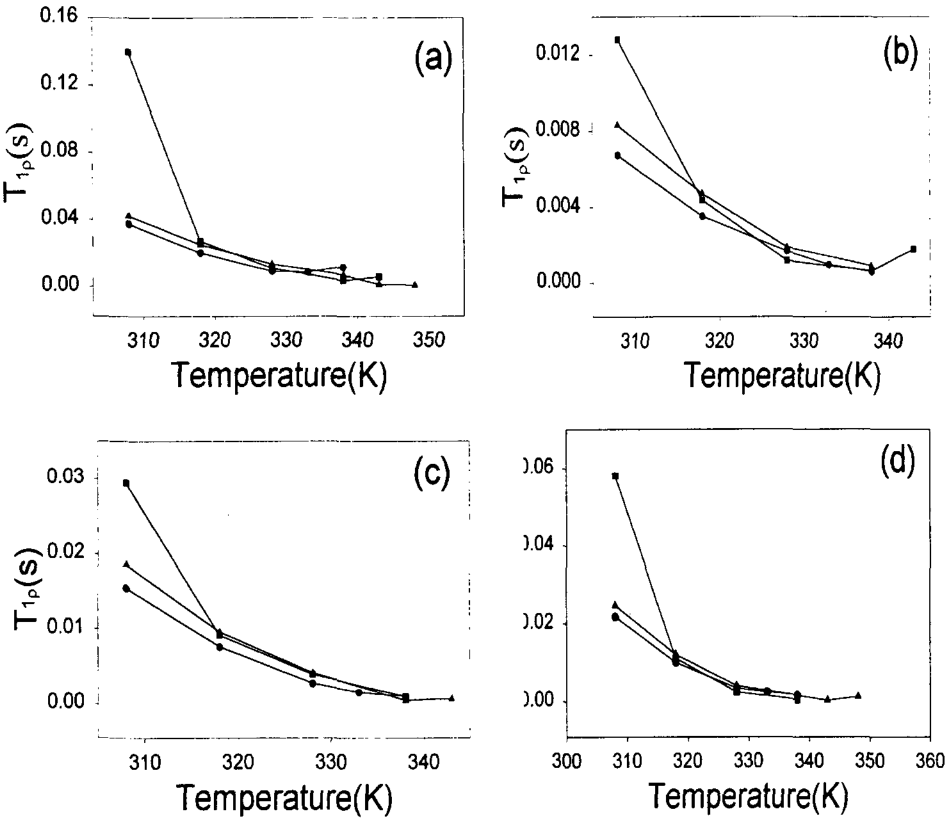

Fig. 5. Temperature dependence of $T_{1\rho}$ of (a) the methyl carbon at 15 ppm, (b) the peak at 38ppm, (c) the peak at 73ppm, and (d) the peak at 102ppm of the PVB with 10 (■), 30 (▲), and 50 w/w %(●) water.

CONCLUSIONS

Dynamics of PVB containing 10~50 w/w % of water were studied with the peak area, line width, and chemical shift in ^{13}C CP/MAS/DD spectra as well as relaxation times (T_1, $T_{1\rho}$) measured over the temperature range 293K – 348K. Water was observed to facilitate molecular dynamics of the PVB molecules overall including conformational exchange of the racemic and meso butyaldehyde rings in the PVB. Therefore macroscopic properties of PVB [Poly(vinyl butyral)] polymer are proved to be correlated with molecular dynamics of the PVB, which in turn, is strongly influenced by the water in the PVB samples. However, the influence of water was not linear to the amount of water in the PVB samples. All our data seem to indicate that water up to 30 w/w % of the sample is closely bound to the PVB polymer, on the other hand, the additional water is relatively free from the PVB polymer. A further study with ^{1}H and ^{2}D NMR techniques would be essential to clarify our current model, which is currently in progress in our laboratory.

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