



Water Content Reduction in Poly(vinyl butylal) during Magic Angle Spinning

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Abstract : Proton magic angle spinning spectra and thermogravimetric analysis data of poly(vinyl butylal) with water in it indicate water contents in the poly(vinyl butylal) samples were reduced during magic angle spinning. Our observation implies that the centrifugal force on the samples due to magic angle spinning cannot be neglected, especially on inhomogeneous and soft samples like poly(vinyl butylal) we tested in this work.

INTRODUCTION

PVB[poly(vinyl butylal)] is well known to be a main ingredient of a plastic interlayer in laminated glass¹⁻² providing resistance to impact and forced penetration, reduction of solar energy transmittance and ultraviolet radiation, and effective control of sound waves. On the other hand, molecular dynamics of PVB has not been well reported. NMR(nuclear magnetic resonance) is one of the powerful analytical methods not only to study overall structure and molecular dynamics of a polymer but also to distinguish each atom's motions³⁻⁴. However, only a few NMR studies on PVB have been reported. NMR spectra of 10% solution of PVB in DMSO-d₆ (dimethyl sulfoxide) elucidated that meso and racemic stereochemical configurations of PVB exist in solution state⁵. Plasticization of PVB by dihexyl adipate studied with MAS ¹³C NMR was reported⁶, where presence of both of meso and racemic stereoisomers in solid state was observed.

One of several PVB synthesis methods is to precipitate PVB into water, which is environmental-friendly and cost-effective^{2,7}. On the other hand, this procedure can result in low acetylation of the initial reaction product and inhomogeneous acetylation distribution over the product^{2,7}. In addition, it is difficult to make PVB with reproducible properties

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after drying the collected PVB from water^{2,7}. This suggests understanding the interaction of water with PVB is essential to have a clue of the optimum drying conditions for reproducible PVB products. Thus we applied solid state NMR, which is very effective to probe the interaction since both of PVB itself and water in PVB can be examined at the same time but separately. But the solid state NMR data themselves were not reproducible due to water content reduction during MAS experiments, which led us to check the spinning effect on the PVB samples by TGA(thermogravimetric analysis) and ¹H MAS experiments.

EXPERIMENTAL

Materials

PVB with nominal 10, 30, 40, and 50 weight percent of water in it, denoted as 10% PVB, 30% PVB, 40% PVB, 50% PVB, respectively, were supplied from the Polymer Research Laboratory, Research Center, Oriental Chemical Industries in Korea. After a long storage time, the measured water contents of the PVB samples by TGA were 4.6, 12.6, 32.7 and 41.5%, respectively.

NMR Spectroscopy

All NMR experiments were carried out on an ^{UNITY}INOVA 600 MHz system (Varian Inc., Palo Alto, U.S.A.) with a 14.1 Tesla wide-bore magnet and a pencil type rotor of 7.5 mm diameter. Sample spinning rate was 4.5 kHz and its stability was within ± 4 Hz for MAS effect. A small amount, 3 ~ 28 mg, of the PVB sample in the rotor was collected each time, at a few hours interval, to detect the water content variation during the sample spinning. The PVB sample stored in a rotor but without sample spinning was examined, too, to make it sure the water reduction is really by spinning.

Proton MAS spectra of the spun samples and the virgin samples were collected at 10 kHz spinning rate with a 4 mm rotor to identify the chemical species variation during sample spinning. Solution 90° pulse length for ¹H was 5 μ s and 2 μ s pulse length, 3 repetition delay, 16 scans were used for obtaining ¹H MAS spectra. All NMR spectra were taken at room temperature. Chemical shift of ¹H NMR was referenced to external neat tetramethylsilane(TMS).

TGA

All TGA data were obtained with a SEIKO SSC/5200H (SEIKO Instruments, Chibashi, Japan) at the Center for Scientific Instruments of Kyungpook National University with about a sample of 3.1 ~ 28 mg loaded in a Pt fan. Temperature was raised up to 600°C at a rate of 20°C/min under nitrogen atmosphere.

RESULTS AND DISCUSSION

Water contents, detected with TGA, of PVB samples with different initial water weight percents versus MAS duration were plotted in Fig. 1. For comparison, the data of the 40% PVB sample kept in a rotor but not spun at all are included. It is clearly shown that the water contents in the PVB samples were dramatically reduced during the first 5-12 hours. Then the water contents seem to be leveled off below 5%.

To check the dependence of water reduction rates on initial water contents in the PVB, relative variation of water amounts to the initial amounts are plotted in Fig. 2. Except the 10% PVB sample, these relative water reduction rates are similar to one another, which implies that chemisorbed water is only about or less than 5% and the rest of water is relatively free to move around and easy to evaporate.

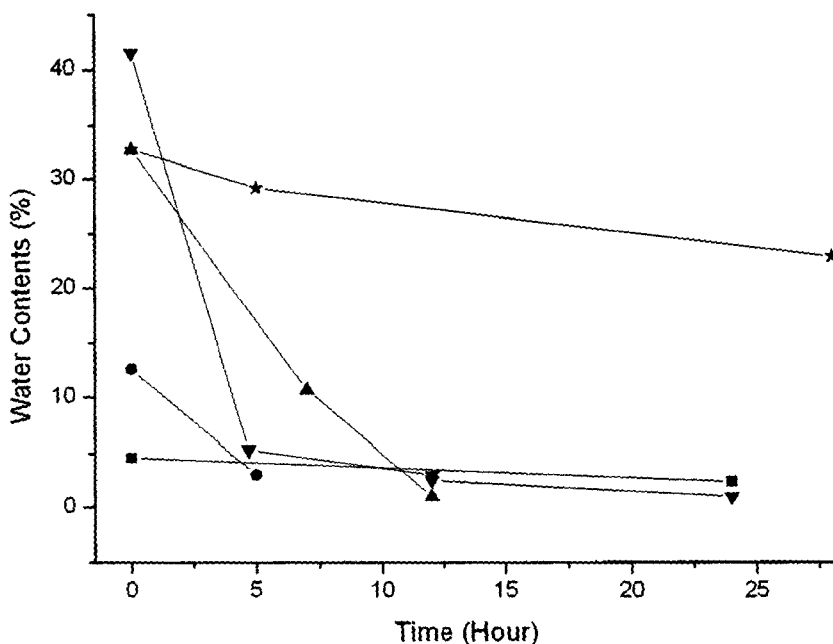


Fig. 1. A plot of water contents, detected with TGA, of 10% PVB (■), 30% PVB (●), 40% PVB (▲), and 50% PVB (▼) samples versus MAS duration. 40% PVB sample kept in a rotor but not spun (★) is also included for comparison.

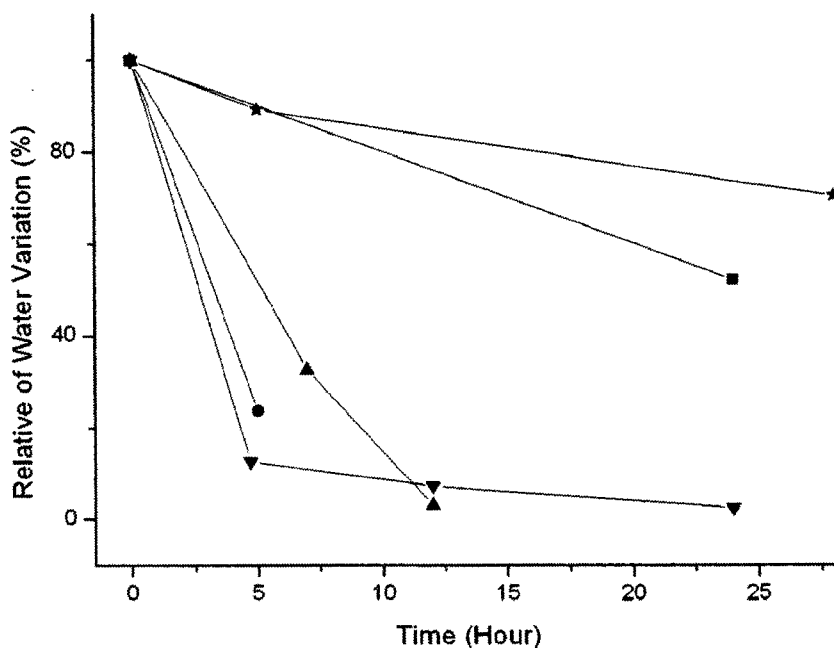


Fig. 2. A plot of relative water contents to the initial ones, detected with TGA, of 10% PVB (■), 30% PVB (●), 40% PVB (▲), and 50% PVB (▼) samples versus MAS duration. 40% PVB sample kept in a rotor but not spun (★) is also included for comparison.

The cap for a pencil type rotor has a pinhole, which may be a main route for water evaporation. However, water of PVB in the rotor with a blocked pinhole was reduced, too. To confirm the result, a rotor plugged with a rotor cap without any pinhole was tested but the result was the same.

Chemical composition change during MAS was identified with ^1H MAS spectra acquired at a 10 kHz spinning rate and 14.1 Tesla. The proton spectra of a 30% PV sample before and after spinning at 4.5 kHz for 24 hours are presented in Fig. 3. The peak near 4 ppm, from free water in PVB, was dramatically decreased after the spinning.

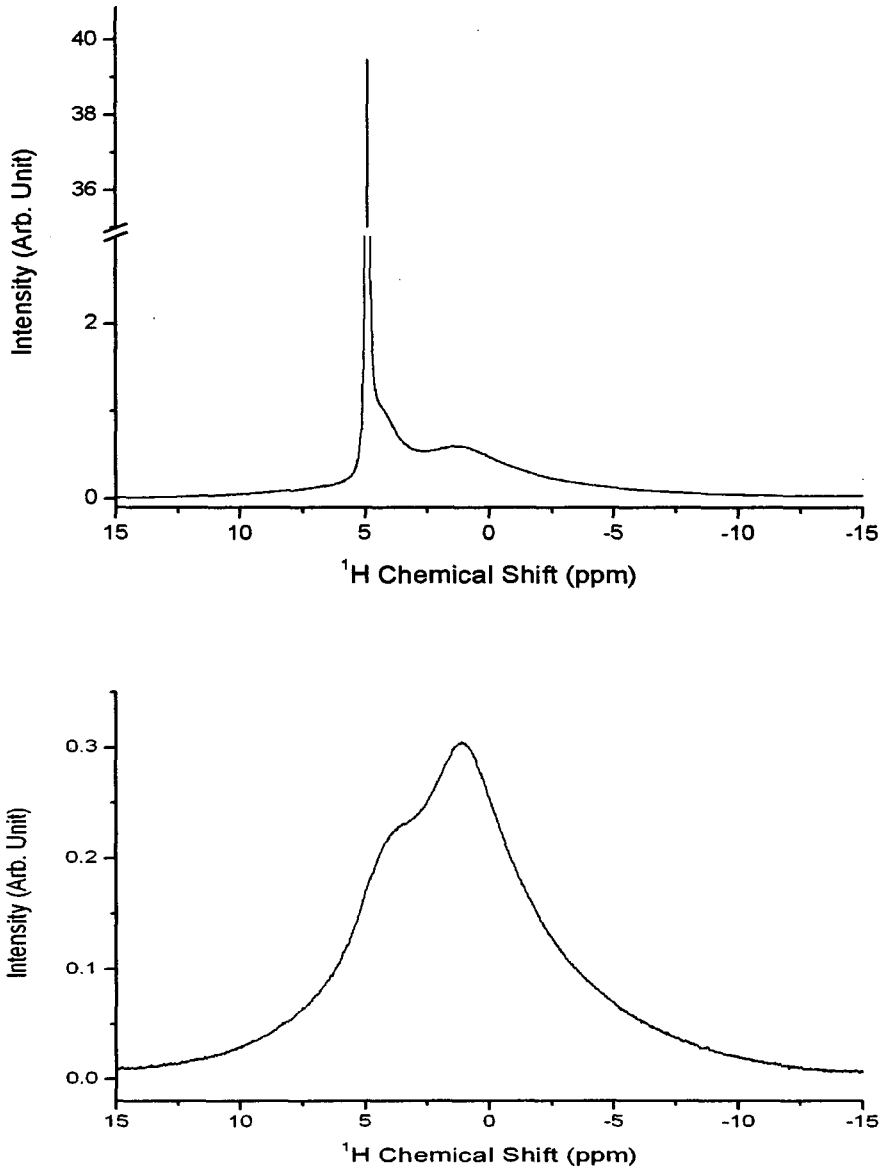


Fig. 3. The proton spectra of 30% PVB sample before (top) and after (bottom) spinning at 4.5 kHz for 24 hours, acquired at 14.1 Tesla and the spinning rate of 10 kHz.

CONCLUSION

The water relatively free in our PVB was easily reduced by sample spinning while bound water was not easily removed. Proton NMR spectra before and after sample spinning clearly showed the decreased peak intensity of water near 4 ppm. Our results indicate centrifugal force on the samples during MAS NMR experiments cannot be neglected, which has been neglected in general, especially on the inhomogeneous and soft samples like our PVB samples.

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REFERENCES

1. <http://www.solutia.com/Products/Saflex.html>
2. T. P. Blomstrom, in "Encyclopedia of Polymer Science and Engineering" (H. F. Mark, Ed.) 2nd ed., vol. 17, p. 137, Wiley-Interscience, 1989.
3. C. A. Fyfe, "Solid State NMR for Chemists" C. F. C. Press, Guelph, Ontario, Canada, 1983
4. F. Laupretre, in "NMR vol 30: Solid State NMR I: Methods" (P. Diehl, F. Fluck, H. Gunther, R. Kosfeld, J. Seelig, Eds.), pp.63-109, Springer-Verlag, Berlin, 1994.
5. M. D. Bruch, J.-A. K. Bonesteel, *Macromolecules*, **19**, 1622 (1986).
6. J. Schaefer, J. R. Garbow, E. O. Stejskal, J. A. Lefelar, *Macromolecules*, **20**, 1271 (1987).
7. Kwang Won Seo, Dukjoon Kim, *Polymer(Korea)* 26, 168 (2002).