# $^{13}$C Solid State NMR Study of the PVC/PEO/GYPSUM SYSTEM

**E. P. Silva, M. A. C. Kaplan**
NPPN/UFRJ, Cidade Universitária, Ilha do Fundão, Rio de Janeiro

**Maria Inês B. Tavares**
IMA/UFRJ, Cidade Universitária, Ilha do Fundão, RJ, CP 68525, Cep 21945-970
**mibt@ima.ufrj.br**

**Abstract:** *Solid state nuclear magnetic resonance spectroscopy (NMR) was used as one of the instrumental method that permits a direct identification of the miscibility of polymer blend components. As a consequence, it also permits to evaluate the homogeneity of the blends at the molecular level. Polymer blends can be used in several applications, thus, it is necessary to have complete understanding of the chemical and dynamic behavior of their components. In this work the solid state NMR results showed that in the system formed by poly (vinyl chloride) (PVC), poly(ethylene oxide) (PEO) and gypsum (PVC/PEO/Gypsum), PEO acts as a plasticizer, but a phase separation occurs due to the weak specific intermolecular interactions among the blend components. Complementary surface information on these blends was obtained by X-Ray Photoelectron Spectroscopy (XPS). From this, it was observed that the blends surface was covered by a continuous PEO layer.*

**Resumo:** *Ressonância magnética nuclear no estado sólido (RMN-MAS) foi usada como um método instrumental que permitiu a identificação direta da miscibilidade dos componentes numa blenda polimérica. Como consequencia, foi possível avaliar a homogeneidade das blendas em nível molecular. As blendas poliméricas podem ser usadas em diferentes aplicações, assim, torna-se necessário ter um completo entendimento do comportamento químico e dinâmico de seus componentes. Neste trabalho os resultados da RMN de estado sólido mostraram que o sistema formado por poli(cloreto de vinilia) (PVC), poli(óxido de etileno) (PEO) e gesso (PVC/PEO/Gesso), PO age como um plastificante polimérico, porém ocorreu separação de fase devido as fracas interações intermoleculares entre os componentes a blenda. Dados complementares sobre estas blendas foram obtidos pela técnica de raio X de superfície (XPS), em que foi observado que na blenda a superfície está recoberta pelo PEO como uma fase contínua e fina.*

## Introduction

Polymer blends can be prepared by different ways, generating materials with specific application. Therefore, to have a response on the evaluation of blend components miscibility it is necessary to apply a methodology of analyses to understand that behavior. Thus, we have chosen solid state NMR spectroscopy, because NMR has several techniques that allow us to evaluate polymeric materials in different time scales. $^{13}$C NMR under MAS technique permits to obtain information about part of sample, by varying acquisition conditions, which only detects the mobile fraction. This generates information on sample molecular mobility in a certain time scale.[1-3] The routine $^{13}$C CPMAS technique informs on changes in sample environment as it depends on the extent of the interaction and the molecular motions, since CP rates depends on the exchange of protons directly attached or of neighboring protons. It is known that mobile carbons atoms take longer to cross polarize than less mobile. Solid state NMR also offers a great variety of relaxation times and they are informative on molecular mobility studies, in distinct time scales.[4-14] The spin-lattice relaxation process is generally dominant in solid state giving direct information on molecular motion. The proton spin-lattice

relaxation time can be measured in the laboratory frame ($T_1$) and in the rotating frame ($T_1\rho$). The proton $T_1\rho$ relaxation time is highly important and used to study segmental dynamic of samples, because it is sensitive to molecular motions in a frequency of tens of kilohertz and also to spin diffusion.[3,11-14] This parameter can be measured indirect from carbons intensity decays employing two experiments, variable contact time (VCT), which on sample mobility and spin-diffusion and delayed contact time (DCT).[3]

The primary purpose of this work was to evaluate the molecular dynamic behavior of the PVC/PEO/gypsum, employing solid state NMR techniques. Another objective is to obtain the blend compatibility, combining of all results.

### Experimental

**Polymer**: commercial PVC and PEO were characterized by ^{13}C solution NMR. PVC was obtained by suspension polymerization and presents atactic configurational sequence distributions and it also presents a predominance of syndiotactic microstructure. The glass transition temperature (Tg) is 85°C. The PEO molecular weight was 400.

**Blends**: blends formed by PVC/PEO/gypsum were prepared by THF solution with different PVC/PEO ratios (80/20, 60/40, 40/60, 20/80 w/w) but the proportion between polymer/gypsum was kept at 90/10 weight by weight, due to the better miscibility of those components. The blends were kept in a dissector for one week and the solvent elimination was accompanied by infrared spectroscopy.

**NMR measurements**: all solid state spectra were obtained on a VARIAN INOVA 300 NMR spectrometer, operating at 75.4 MHz for [13]C. The solid experiments were obtained at ambient probe temperature and were performed using gated high decoupling. A zirconium oxide rotor of 7mm diameter was used to acquire NMR spectra at rates of 6 kHz. The MAS ^{13}C NMR spectra were carried out using short recycle delay time (0.3s) between 90 degrees pulse and CPMAS ^{13}C NMR with 2s as a recycle delay time[5]. For variable contact-time experiment, the same conditions for CPMAS were used and a range of contact time was established from 0.2 to 8ms. The delayed contact time was carried out with a spin-locking range varied from 0.2 to 8 ms.

### Results and Discussion

The ^{13}C MAS NMR blends analyses showed that mobile region is formed by at least two domains: one constituted by plasticized PVC, with PVC signals located at (57.7 ppm – CH-Cl and 47.7 ppm – $CH_2$) and the other one rich in PEO (with the signals located at 71 ppm - $CH_2$-O). This observation was also confirmed by the XPS analysis that evaluates the nucleus in the blends surface. The results showed that only PEO was detected in the surface, indicating that PEO is covering the sample as a continuous layer.

The profile of ^{13}C CPMAS spectra informed on ^{13}C signals decays, which can be extrapolated to the component distribution. Thus, up to 40% of PEO in the blends, only two wide signals from PVC located at (57.6 ppm, CH) and 47.0 ppm ($CH_2$) were detected. As the PEO content increases to 60% both

PVC and PEO (71.2 ppm) signals were detected (Figure 1). The distribution form of the $^{13}$C signals of PVC, PVC/PEO 60/40 and PVC/PEO 40/60 are presented in Figure 2. From the analysis of VCT spectra, changes in the carbon decays profile showed a non- linear decays for both polymer blend components, indicating an existence of heterogeneous phase in those blends, as a consequence three different domains could be observed one rich in PVC, other rich in PEO and a third one a plasticized PVC, confirming what was already detected by $^{13}$C MAS technique.
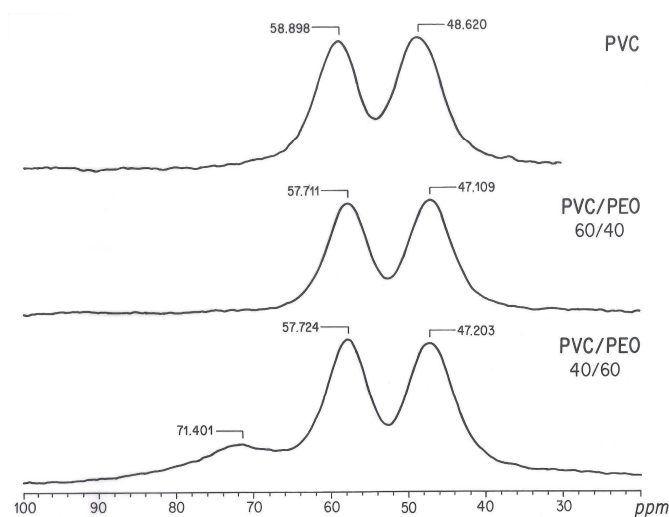


**Figure 1.** $^{13}$C CPMAS NMR spectrum for PVC, PVC/PEO 60/40 and PVC/PEO 40/60, obtained by VTC experiment, for the ternary blends
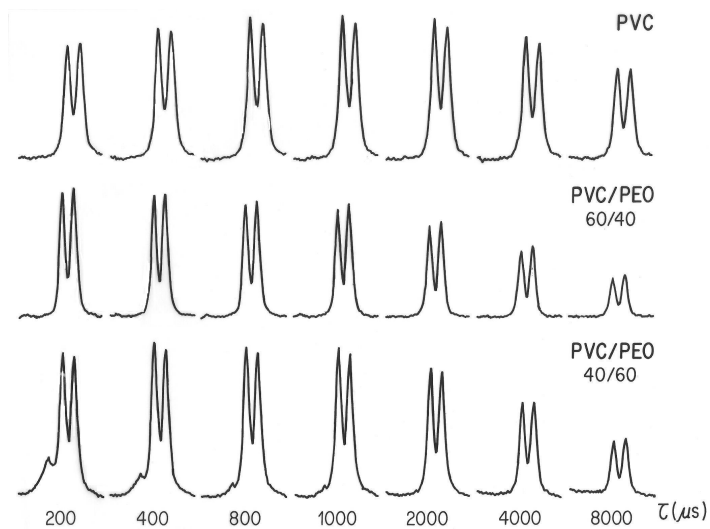


**Figure 2.** Distribution form of the signals for the VCT for PVC, PVC/PEO 60/40 and PVC/PEO 40/60, focusing the decay of $^{13}$C signals in a series of CPMAS $^{13}$C spectra

The evaluation of blends dynamic behavior was carried out using proton spin-lattice relaxation time in the rotating frame. The values obtained for this parameter, focusing the PVC polymer, were determined by two techniques: variable contact time that could inform on spin-diffusion and domain mobility (Table 1), and by delayed contact – time, which generated information on chains homogeneity and the dispersity in matrix (Table 2).

**Table 1.** $T_1{}^H\rho$ values of PVC/PEO/gypsum, for PVC signals, measured by VCT

| PVC/PEO/gypsum | $T_1{}^H\rho$ (ms) | |
|---|---|---|
| | 57 | 47 |
| 100/0/0 | 2 | 2 |
| 90/0/10 | 4 | 4 |
| 80/20/10 | 5 | 8 |
| 60/40/10 | 6 | 6 |
| 40/60/10 | 7 | 8 |
| 20/80/10 | 4 | 5 |

From the $T_1{}^H\rho$ values, obtained by the variable contact time experiment, listed in Table 1, one can see that all systems presented different mobility compared with PVC it self (which presents lower values of this parameter, because its chains proximity). However, in 90/10 and 80/20 compositions a plasticization process is taking place, as the average intermolecular distance of blend components increased (the relaxation data also increased). For 60/40 ratio, the values of $T_1{}^H\rho$, indicates that in this ratio a reduction of the average intermolecular distance and the molecular motion of each component was also changed. As the quantity of PEO increased to 60 and 80% a non linear behavior of $T_1{}^H\rho$ values suggested a phase separation and consequently the formation of domains rich in both polymers.

**Table 2.** $T_1{}^H\rho$ values of PVC/PEO/gypsum, for PVC signals, measured by DCT

| PVC/PEO/gypsum | $T_1{}^H\rho$ (ms) | |
|---|---|---|
| | 57 | 47 |
| 100/00/0 | 2 | 2 |
| 70/00/10 | 4 | 5 |
| 80/20/10 | 5 | 5 |
| 60/40/10 | 4 | 4 |
| 40/60/10 | 5 | 5 |
| 20/80/10 | 4 | 5 |

The values of $T_1^H\rho$ parameter, measured by DCT, confirmed the results obtained by VTC experiment, the same behavior was found.

Comparing the $T_1^H\rho$ parameter behaviors, focusing both experiments, it is clear that no strong interaction process is occurring in the blends ratios. This fact can, probably, come from the mixture process and also from the PVC characteristics.

**Conclusion**

Based on the primary purpose of this work, NMR spectroscopy has contributed to understanding the blends behavior in its length of scale, showing in this polymer blend the components present some miscibility at the molecular level.

**Acknowledgements**

**References**

1. R.K. Harris, NMR studies of solid polymer, in Polymer Spectroscopy, Ed., A.H. Fawcell, John Wiley & Sons, England (1996).

2. F.A. Bovey; P.A. Mirau "NMR of Polymers", Academic Press, New York (1996).

3. N.M. Silva M.I.B. Tavares *J.Appl.Polym.Sci*. **60** (1996) 663.

4. D.A. Costa; C.M.F. Oliveira; M.I.B. Tavares *J. Appl. Polym. Sci*., **69** (1998) 129.

5. E.P. Silva; M.A.C. Kaplan; M.I.B. Tavares, *J. Appl. Polym. Sci*., **in press.**

6. R.A. Komoroski "high Resolution NMR Spectroscopy of synthetic Polymers in Bulk", VCH Publishers, Deerfield Beach (1986).

7. V.McBrierty; K.J. Parker "Nuclear Magnetic Resonance in Solid Polymers", Cambridge University Press, Great Britain (1993).

8. E.O. Stejskal; J.D. Memory "High resolution NMR in the Solid State", Oxford University Press, New York (1994).

9. J.K.M. Sanders; B.K. Hunter "Modern NMR Spectroscopy A Guide for Chemists", Oxford University Press, Oxford, 2 Ed. (1996).

10. K. Schmidt-Rohr; H.W. Spiess "Multidimensional Solid-State NMR and Polymers", Academic Press, New York (1994).

11. N.M. Silva; M.I.B. Tavares; E.O. Stejskal *Macromolecules*, **33** (2000) 115.

12. A. Simmons; A. Natanshon *Macromolecules* **24** (1991) 3651.

13. T. M. F. F. Diniz; M.I.B. Tavares *J. Appl. Polym. Sci*., **100** (2006) 1492.

14. M.Preto; M.I.B. Tavares; E.P. Silva, *Polymer Testing* **26** (2007) 501.