Determination of the miscibility of phosphorus additives in polymer matrices by high resolution solid state NMR

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SUMMARY
        The measurement of high resolution solid state NMR proton $T_{1\rho}$ values (relaxation time in the rotating frame) provides a method for the study of the compatibility of phosphorus additives with polymer matrices. Results are compared for two commercial phosphorus stabilizers, bis (2,4 di-t-butylphenyl) pentaerythritol diphosphite (Phosphite 1) and tris (2,4 di-t-butylphenyl) phosphite (Phosphite 2), in 5% masterbatches in linear low density polyethylene (LLDPE). Phosphite 1 shows compatibility even when poorly mixed while the Phosphite 2 shows separation into two domains with different relaxation rates and different chemical shifts in the solid state.

INTRODUCTION
        Proton $T_{1\rho}$ values (proton decay rate constants in the rotating frame) of two blended materials are averaged to a single value by
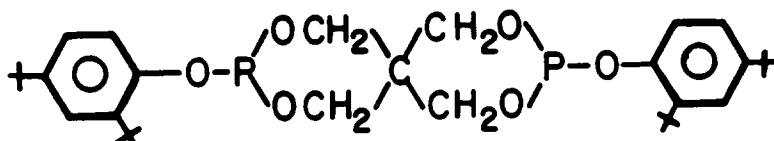
PHOSPHITE 1
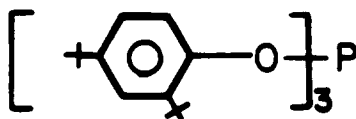
PHOSPHITE 2

spin diffusion if there is extensive intermixing of the two components at the nanometer level. Thus if two materials are very miscible, they will both have similar $T_{1\rho}$ values in a blend as measured by solid state proton NMR relaxation studies. The linearity of the observed decay rates, moreover, provides qualitative information about the homogeneity of the mixture.

With high resolution solid state NMR using cross polarization techniques, the proton $T_{1\rho}$ decays can be monitored indirectly through other nuclei (e.g. phosphorus or carbon) in the vicinity of the protons. This method provides more useful information then would be obtained from the solid state proton NMR itself. Stejskal (1,2) and coworker, for example, have used high resolution carbon-13 NMR to study the compatibility of solid polymeric blends such as polystyrene and polyphenylene oxide.

This report extends the technique to the study of the miscibility of phosphorus additives in polymer matrices using high resolution phosphorus-31 solid state NMR. Through cross polarization the intensity of the phosphorus signal mirrors the decay rate of the protons in proximity with the phosphorus. Moreover, no interfering NMR signals are observed from the polymer itself, allowing moderately low levels of the additive to be monitored. Attached results are presented for 5% masterbatches of Phosphite 1 and Phosphite 2 in linear low density polyethylene.

EXPERIMENTAL AND CALCULATIONS

Phosphorus-31 and carbon-13 high resolution solid state NMR were recorded on a JEOL FX 60QS NMR spectrometer employing standard cross polarization magic angle spinning pulse sequences. Observe frequencies were 24.2 MHz for phosphorus-31 and 15.0 MHz for carbon-13. Spinning of the sample was at the magic angle at spinning rates of around 2KHz. Spin locking conditions were achieved with carbon and proton, or phosphorus and proton, rotating frame fields of around 42 KHz. Contact time (in milliseconds) between the carbon or phosphorus and the protons were varied from 0.25 to 12.0 msec to monitor the decay of the protons. A semilog plot of peak intensity at long contact times versus the variable contact time allowed calculation of the proton $T1_{\rho}$ decay constant according to the formula:

$$I_t = I_o \, e^{-t/T_{1\rho}} \qquad (1)$$

where I_t is the peak intensity at contact time t and I_o is the maximum peak intensity (usually at t = 2 – 4 msec). Linear regression analysis was used to obtain the best slope as well as the correlation coefficient (linearity of the decay).

The 5% masterbatches were prepared by extrusion compounding. One masterbatch, however, was prepared by dry blending. Phosphite 1 is commercially available as Ultranox[R] 626. Phosphite 2 is a laboratory preparation of TBPP (tris(2,4-di-t-butylphenyl)-phosphite) commercially available as Irgafos[R] 168 and Hostanox[R] VP PAR. The LLDPE was Union Carbide GRSN 7042.

RESULTS-PHOSPHITE 1

Figure 1 depicts the rotating frame relaxation behavior of the phosphorus-31 NMR signal from Phosphite 1 with respect to the contact time. Table 1 presents the values for the proton $T_{1\rho}$ obtained by phosphorus-31 and carbon-13 high resolution solid state NMR for Phosphite 1, LLDPE, and 5% masterbatches of Phosphite 1 in LLDPE. One masterbatch was prepared in the usual manner (by extrusion compounding) while the other was merely dry blended.
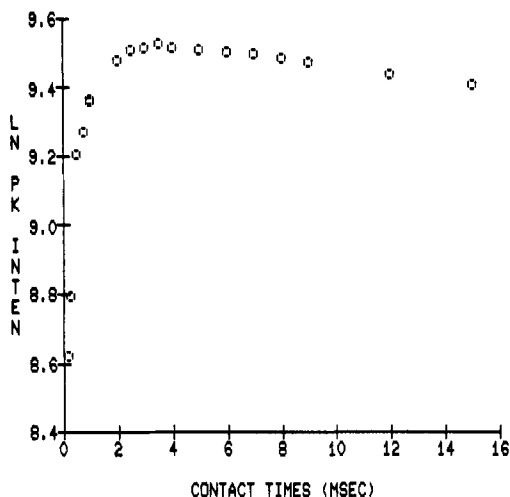
Figure 1. Proton rotating frame relaxation behavior of phosphite 1 monitored by phosphorus-31 NMR. The proton $T1_\rho$ constant is calculated from the reciprocal of the slope of the decay portion of the graph after the peak maximum (around 3.5 msec in this case).

Table 1
Proton rotating frame relaxation times $(T1_\rho)$ for
Phosphite 1/LLDPE Masterbatch

Substance	Nuclei Monitored	$T_{1\rho}$ (H) msec	Corr. Coeff.
Phosphite 1	P-31	98.2 ± 0.2 [a]	0.99 ± 0.01 [a]
LLDPE	C-13	12.0 ± 0.2	0.99 ± 0.00
Phos.1/LLDPE [b]	P-31	16.2	0.93
Phos.1/LLDPE [c]	P-31	11.0 ± 0.8	0.96 ± 0.02

a) Average deviation in the case of duplicate measurements b) Extrusion compounded c) Dry blended.

Phosphite 1 shows a proton $T_{1\rho}$ of 98.2 msec by phosphorus-31 NMR (the spiro pentaerythritol diphosphite phosphorus signal was used at 117 ppm downfield from computer reference $CaH_4(PO_4)_2 \cdot H_2O$). The LLDPE by carbon-13 (ethylene chain signal) has a much faster proton decay in the rotating frame with a $T_{1\rho}$ value of 12 msec. In the 5% masterbatches, however, the proton $T1_\rho$ value for Phosphite 1 has become quite close to that of the LLDPE reflecting good compatibility with the polymer. The dry blended masterbatch also showed the same effect indicating that even with minimal mixing Phosphite 1 is readily dispersed in the LLDPE. All decay rates appeared linear with correlation coefficients between 0.93 and 1.0 with most over 0.97.

RESULTS-PHOSPHITE 2
The results on Phosphite 2 on the other hand were quite different from those for Phosphite 1. Phosphite 2 shows a single peak in the solid state phosphorus-31 NMR at 154 PPM downfield from the $CaH_4(PO_4)_2 \cdot H_2O$ reference (computer reference). In solution, however, Phosphite 2 shows a markedly different chemical shift of approximately 131 ppm downfield from 85% phosphoric acid. Such a large difference in the chemical shift between the solid and the solution phosphorus-31 NMR is unusual.

In the 5% masterbatches, however, both chemical shifts appear, one at 154 ppm and the other at 133 ppm downfield from the calcium phosphate. The first is postulated to represent domains of solid undispersed Phosphite 2 while the second upfield peak represents Phosphite 2 dissolved in the LLDPE. Preliminary relaxation studies (phosphorus-31 NMR) appear to confirm this interpretation of the two chemical shifts. Phosphite 2, as well as competitive versions of this material, show quite long proton $T_{1\rho}$ values (greater than 500 msec). Due to instrumental limitations, however, the long $T_{1\rho}$ values cannot be measured accurately on the FX60QS due to the possibility of overheating in the probe. It appears, however, that in the 5% masterbatches in the LLDPE the two phosphorus-31 signals have different relaxation times. The signal at 154 ppm appears to be the slower relaxing species, and therefore less intimate contact with the matrix. The phosphorus, on the other hand, with the chemical shift at 133 ppm has a proton $T_{1\rho}$ on the order of magnitude as the LLDPE itself, evidence of closer interaction with the LLDPE matrix.

CONCLUSIONS

Results from both chemical shifts and relaxation studies appear to show a difference in the miscibility of the Phosphite 1 and 2 in 5% masterbatches in LLDPE. Phosphite 1 forms a homogeneous dispersion in the LLDPE at this level while Phosphite 2 exhibits a segregation into domains of pure Phosphite 2 and dissolved Phosphite 2. Caution, however, must be taken in extrapolation of these results to other levels of Phosphite 1 or 2 in LLDPE. The data may only be an indication that a 5% loading exceeds the solubility of Phosphite 2 in LLDPE. Higher field instruments would allow observation of lower levels of the additives. Nevertheless, it is evident that this method shows promise in examining the relative dispersion of phosphorus containing additives in polymer matrices.

REFERENCES

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2. Schaefer, J., et al, Polym. Prepr. Am. Chem. Soc., Div. Polym. Chem. 20, 247 (1979).

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