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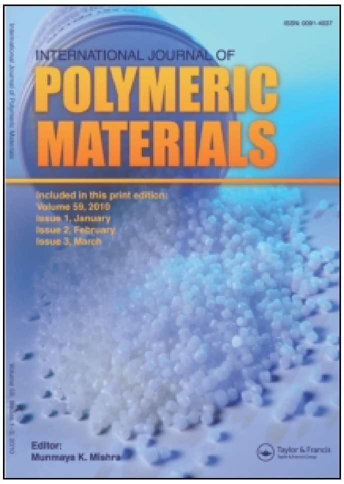

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Evaluation of Composites Miscibility by Low Field NMR

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Solid state nuclear magnetic resonance (NMR) is a powerful technique to analyze polymer composites. The use of proton relaxation data to evaluate the dispersity of the dispersion phase in the composite and its homogeneity are very wide. In this work PVC/silica composites were prepared using different ratios to obtain a new material to be used in chromatograph column for separation of plant extracts. Thus, this study used proton spin–lattice and spin-spin nuclear magnetic resonance relaxation data, determined in a low field NMR spectrometer as a method to characterize those composites in relation to silica dispersion as well as PVC/silica compatibility. From the relaxation data analyses, the best ratio of PVC/silica, according to the components dispersion and consequently composite compatibility, was 80/20, according to the determined T_1 *values.*

Keywords: compatibility, composite, low field NMR

INTRODUCTION

It is very well known that composite materials are engineered materials made from two or more constituent materials with significantly different physical or chemical properties, which maintain their separate and distinct characteristics.

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In composites, there are two major types of constituent materials: matrix and reinforcement. The matrix material surrounds and supports the reinforcement material to maintain their position in the new structure. The reinforcements are used to impart special physical properties, such as mechanical and electrical for example, with the objective to enhance the matrix properties [1–2]. Due to the wide variety of matrix and reinforcement materials available, the design potential is wide. This great variety has resulted in an enormous amount of research all over the world, and consequently a necessity to better characterize the new structures formed and the compatibility of both composite components. This made scientists use different techniques, among which spectroscopic methods have been very much used, because they inform on the interaction process and structure modifications [1–10].

Engineered composite materials must be formed to shape new products. This involves strategically placing the reinforcements in the matrix, which affects its properties. A variety of methods to prepare a composite are used according to the end item design requirements. These fabrication methods are commonly called molding or casting processes. The principal factors impacting the methodology are the nature of the chosen matrix and reinforcement materials [1–4].

PVC composites can be formulated using various types of filler, which are normally chosen according to the product that will be prepared from these composites [2–6]. Inorganic fillers have been very much used to obtain composite with special properties and applications. PVC is a thermoplastic polymer that combines very well with inorganic compounds. Silica is one of the inorganic filler that presents some compatibility with PVC, as both possess intermediate polarities. The introduction of silica in the PVC matrix can promote composition with some ordered regions with mesoporosity, suggesting the formation of more ordered structures, which imparts a significant influence on the final properties of PVC and its processability. The influence of the hydroxyl silica groups has been studied with regard to being a bridge to link the inorganic compound to organic compound, and for providing a valuable feedback on how the composites are performing.

NMR offers a great variety of relaxation times that may provide very good information for the study of the interface interaction between both composite components and the inorganic particle dispersion. This may be obtained by the use of low field NMR to determine the proton spin–lattice (T_1) and spin-spin (T_2) relaxation times [3–10].

Consistent with the aforementioned, the main purpose of this work is to prepare compatible PVC/silica composites, to be used in chromatography column, and also to develop their characterization by proton nuclear magnetic resonance, using a low field NMR spectrometer. The significance of this work is to demonstrate how useful the use of low field NMR can be to better characterize composites, especially PVC/silica composite.

EXPERIMENTAL

Samples

Commercial PVC prepared by suspension (supplied by Solvay industry) and silica (Si) (supplied by Merck) were blended in solution using tetrahydrofuran as solvent. The films of PVC/Si were prepared at different ratios (80/20, 60/40, 40/60, and 20/80) by solution casting onto plates and the solvent was eliminated slowly during a week. After that, these films were put into an oven with circulating air for three days at 40°C to completely eliminate the solvent residues. The solvent elimination was accompanied by the disappearance of its peak in the infrared spectrum.

NMR Measurements

Low field NMR Resonance MARAN ultra 23 was used for the relaxation measurements. Proton spin–lattice relaxation times were determined directly by the traditional inversion-recovery pulse sequence (delay 180°-τ-90° acquisition) using 20 data points for a range of τ, which varied from 0.1 to 10,000 ms, with a recycle delay at 10 s and 4 scans for each point. The spin-spin relaxation times were also determined using a Carr-Purcell-Meiboom-Gill (CPMG) pulse sequence (delay 90°-τ-180° acquisition) with τ 100 µs, recycle delay 5 s and 9600 scans. The relaxation values and relative intensities were obtained by fitting the exponential data with the aid of the WINFIT. Distributed exponential fittings, as a plot of relaxation amplitude versus relaxation time, were performed by using the WINDXP software.

RESULTS AND DISCUSSION

According to the purpose of this work, the proton T_1 (Table 1) and T_2 (Table 2) data were recorded to evaluate the interaction between both composite components as well as the dispersion of the inorganic filler in the amorphous region, in order to evaluate the composites' compatibility.

From the proton spin–lattice relaxation time measurements showed in Table 1, the composite with PVC/Si 80/20 ratio presented good

TABLE 1 Proton Spin–Lattice Values of the PVC, Silica (Si), and PVC/Silica (PVC/Si) Composites, Measured by Low Field NMR

PVC/Si	T_1H (ms)	Intensity (%)
100/0	343.0	25
	708.4	38
	861.8	37
80/20	237.2	27
	668.2	36
	803.5	37
60/40	17.7	13
	363.0	27
	713.0	60
40/60	19.1	17
	459.1	38
	699.1	45
20/80	12.3	22
	45.6	19
	563.0	59
0/100	15.7	62
	106.4	38

TABLE 2 Proton Spin-Spin Values of the PVC, Silica (Si), and PVC/Silica Composites, Measured by Low Field NMR

PVC/Si	T_2H (ms)	Intensity (%)
100/0	14.7	31
	98.0	37
	513.7	32
80/20	0.9	87
	22.7	9
	178.5	4
60/40	1.4	89
	25.1	9
	270.2	2
40/60	0.9	91
	17.6	7
	149.6	2
20/80	1.4	88
	10.4	9
	112.7	3
0/100	0.8	92
	11.8	6
	121.9	2

components dispersion and compatibility, because the T_1 values have a small decrease due to the interfacial bonding strength between the composite components. For the others ratios, no good interaction between the blend components was observed, due to the large changes in the values of proton spin–lattice and also a detection of silica T_1 value. However, for all PVC/Si ratios the rigid domain, which presents the high value of relaxation parameter, controls the relaxation process, because T_1 parameter predominates in relation T_2.

The measurements of proton transverse magnetic relaxation were made in pure PVC, silica, and their composites at different ratios (see Table 2). These relaxation times were found to conform and/or complete the spin–lattice relaxation time information on the composites being evaluated.

It was found that only the rigid component contributes to the T_2 values, according to the percentage intensity of domains, showing that the composite relaxation mechanism is controlled by the PVC domain, which is probably a dominant rigid phase. The spin-spin relaxation rate was found to decrease markedly during the PVC modification by silica incorporation. Comparing to pure PVC, all PVC/silica ratios was influenced very much by the silica incorporation and there is some interaction in the system, in spite of the fact that all compositions were heterogeneous and a phase separation would be detected, especially after 40% or more silica were added.

CONCLUSIONS

In this work it was found that the same information is extracted from inversion–recovery (T_1) and CPMG (T_2) relaxation curves, and it was shown that the NMR relaxometry is a nondestructive technique that allows the evaluation of the composite components interactions and obtaining an insight into the behavior of the system in relation to its molecular mobility. The techniques used were also precise and rather efficient.

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