Contents lists available at ScienceDirect

# Polymer Testing

journal homepage: www.elsevier.com/locate/polytest

Test method

# The use of relaxometry to evaluate the aging process in hybrid HIPS nanocomposites

Paulo Sergio Rangel Cruz da Silva, Maria Inês Bruno Tavares[*]

Centro de Tecnologia, Instituto de Macromoléculas Professora Eloisa Mano — IMA, Universidade Federal do Rio de Janeiro — UFRJ, Bloco J, Ilha do Fundão, CP 68525, 21945-970 Rio de Janeiro, RJ, Brazil

ABSTRACT

Nuclear magnetic resonance allows measurement of proton spin-lattice relaxation times, which reflect the molecular mobility of the sample according to the changes in its chemical structure caused by different mechanisms that can be induced. Nanomaterials and their derivatives are good systems to investigate through NMR relaxometry due to their particular organization and intermolecular interaction. In this study, NMR relaxometry was employed to evaluate UV aging of HIPS nanomaterials formed by the solution method. The results obtained were quite interesting. Regardless of organoclay amount, the aging effect occurred slowly up to 200 h of UV light exposure. However, at 300 h of UV light exposure, competition between chain degradation and chain recombination occurred, and at 400 h the aging effect increased the chain scission.

© 2015 Elsevier Ltd. All rights reserved.

## 1. Introduction

The exposure of polymers to oxygen or ozone or both causes aging, which is intensified by ultraviolet light [1,2]. This is one of the most significant factors in weathering of polymers, because it is an accelerated process that promotes chemical change in the polymer chains, reducing their molecular weight and making the material more brittle. This reduces tensile strength as well as impact strength and elongation [1–10]. Measurement of these changes provides information on the behavior of materials and the intermolecular interaction forces that promote nanoparticle dispersion and distribution in the polymer matrix [11–16].

Among the various techniques other than mechanical properties that can be used to investigate the aging process, one of the best to investigate molecular changes is nuclear magnetic resonance spectroscopy (NMR), because it permits monitoring the evolution of these changes in the solid state [17–22]. In solid-state NMR, there are many techniques that are helpful to detect chemical changes or other modifications in the polymer matrix. One of the more suitable techniques to understand the molecular changes inside a solid material is NMR relaxometry, which allows evaluating small chemical changes in different molecular systems, including nanomaterials. Relaxometry is also a good technique because it is nondestructive, so the sample can be analyzed in its intact form [23–33].

The objective of this work was to detect the changes caused by UV aging in complex nanocomposites by applying NMR relaxometry, because it offers the unique possibility of probing dynamics according to the rigid and mobile phases. NMR relaxometry can be an alternative method to evaluate and understand the effect of organoclay ratio and dispersion in hybrid systems.

The use of NMR relaxometry involving proton spin-lattice relaxation time was, for the first time, applied to the study of sample aging. We not only used the values of relaxation, but also the domain relaxation curves that have not previously been used for this purpose. The use of both relaxation data, that is appropriate for molecular motion changes and domain curves, gives us complementary information about the degradation and recombination processes.

NMR can measure a great variety of relaxation times. Proton spin-lattice relaxation time measurements are generally used to identify the heterogeneity of polymer materials containing domains with size of about ~25 to >50 nm [17–23,26–33]. The relaxation time ($T_1$) provides information about the miscibility and the domain size of various phases in the polymer system. This analysis enables identification of the molecular motions and domain formation through the changes promoted in the proton

* Corresponding author.
  E-mail addresses: rangel@ima.ufrj.br (P.S.R.C. da Silva), mibt@ima.ufrj.br (M.I.B. Tavares).

relaxation times. This feature makes the technique suitable for analyzing the molecular dynamics of polymer systems and materials, especially nanocomposite materials. The proton spin-lattice relaxation time is highly sensitive to molecular dynamics, related to fast movements [23—33]. Any alteration in the molecular dynamics causes changes in the relaxation time values. When clay lamellae are well dispersed and distributed in the polymer matrix, at least two main nanostructures can be formed, commonly termed exfoliated and intercalated. In most cases, a combination of both nanostructures is found in nanostructured materials. Generally speaking, when the exfoliation process is predominant, the relaxation time decreases compared to that of the pure polymer matrix, due to the paramagnetic clay effect, which comes from paramagnetic metals (e.g., iron) in the polymer structure. These metals act as relaxing agents and cause a decrease in the value of this parameter, related to the quantity of the exfoliated clay lamellae and also the interaction between clay lamellae and polymer chains. The reduction in the spin-lattice relaxation time is caused by the increase in the molecular movements of the polymer chains due to the freer chain movement at the surface of the layers. Increased relaxation time means that the polymer chains are constrained between the clay lamellae, restricting their movements, leading to the formation of a predominantly intercalated structure. In turn, reduction of the proton relaxation time indicates exfoliation because of less restriction of movement [26—33].

## 2. Experimental

### 2.1. Materials

Commercial organically modified montmorillonite clay (OMMT) which is modified with dimethyl benzyl hydrogenated tallow ammonium (DMBHTA) was acquired from Bentec (Viscogel S7). Commercial high-impact polystyrene in solid pellet form containing 5% polybutadiene and having a glass transition temperature of 98 °C was purchased from Innova S.A. Chloroform and toluene were used as the casting solvent pair.

### 2.2. Nanocomposite preparation

The polymer was dissolved in a 250-mL Erlenmeyer flask with 50 mL of chloroform and 100 mL of toluene, under mechanical stirring. The clay mass (dispersion) was added to the polymer solution (containing 5% wt%). The desired amount (1, 2 and 3% w/w) of OMMT was weighed and dispersed in 50 mL of chloroform by mechanical stirring for 24 h. After obtaining a homogeneous mixture, the clay dispersion was stirred for a further 24 h, and then poured into the polymer solution. The resulting mixture was put into a Petri dish (150 mm diameter) and the dishes then placed in an oven for 24 h at ~40 °C to remove the solvents and produce the films. HIPS films were also obtained as described above without adding the OMMT, for comparison. The sample codes take into consideration the pair of solvents used (HTC) and the proportion of organoclay used, varying from 0 to 3% w/w (HTC0, HTC1, HTC2 and HTC3) [29].

### 2.3. NMR relaxation measurements

The $^1$H NMR relaxation measurements were performed in a Maran Ultra 23 low-field NMR spectrometer, operating at 23.4 MHz (for protons) and equipped with an 18-mm variable temperature probe operating at 300 K. Proton spin-lattice relaxation time ($T_1H$) was measured with the inversion-recovery pulse sequence ($D_1 - \pi - \tau - \pi/2 - $ acquisition), using a recycle delay value of $5T_1$ (e.g., D1 of 5 s), and the $\pi/2$ pulse of 7.5 ms was calibrated automatically by

the instrument's software. The amplitude of the FID was sampled for 40 $\tau$ data points, ranging from 0.1 to 5000 ms, with 4 scans each point. The data were processed using the Winfit program with the aid of WinDXP software, which comes with the equipment.

## 3. Results and discussion

### 3.1. NMR relaxation data

The evaluation of the systems before and after UV aging was done by NMR relaxometry, employing proton spin-lattice relaxation time in the laboratory frame, determined in a low-field NMR. This parameter was analyzed in terms of clay ratio for the same time of UV light exposure. First, the NMR relaxation data were investigated before the samples were submitted to the aging process.

Table 1 shows the proton spin-lattice relaxation times for HTC samples before being submitted to UV aging.

The analyzed nanocomposites had shorter relaxation times than the pure polymer matrix. A very important factor for this behavior is the structure formed by the clay and matrix. For materials that contain intercalated structure, the rotational freedom of the polymer chains that are located between the lamellae is limited, causing an increase in the relaxation time. Therefore, a decrease in relaxation time in this material shows the predominance of an exfoliated structure, which allows greater rotational freedom for polymer chains, in addition to the influence of the paramagnetic metal present in the clay structure, which aids the relaxation process and reduces the relaxation values. These results were used as the basis for comparison with the materials obtained after being submitted to UV light.

Table 2 contains the proton spin-lattice relaxation times for HTC samples after being submitted to UV aging for 100 h.

Table 2 shows the increase in relaxation times for all compositions after 100 h of UV light exposure. This increase follows the variation of the clay percentage. Due to the very low percentage, it is not possible to attribute this variation of $T_1$ to the influence of paramagnetic metals. Probably, this difference is related to different percentages of intercalated and exfoliated structure at each concentration. However, all materials have mixed structure. The increase in the relaxation times indicates decreasing mobility of the system, which may have been generated by recombination of chains, increasing the molecular weight, or by the degradation of smaller chains.

Table 3 gives the proton spin-lattice relaxation times for HTC samples after UV aging for 200 h.

The relaxation data in Table 3 show that the HTC1 and HTC0 systems have nearly the same relaxation times. This suggests that the HTC1 sample suffered a reorganization of the clay lamellae, tending to reassembling after 200 h of UV light exposure. However, the pure polymer matrix presents a significant decrease in $T_1$ when compared to the HTC0-100h sample, suggesting that the matrix began to degrade. It can also be noted that the HTC2 and HTC3 samples were not modified after doubling the exposure time, indicating that the clay acts as a barrier to UV light due to its

**Table 1**
Values of proton spin-lattice relaxation time for HTC samples before UV aging.

| Sample − exposure time | $T_1$ (ms) ($\pm 2\%$) |
| --- | --- |
| HTC0-000h | 570 |
| HTC1-000h | 540 |
| HTC2-000h | 519 |
| HTC3-000h | 513 |