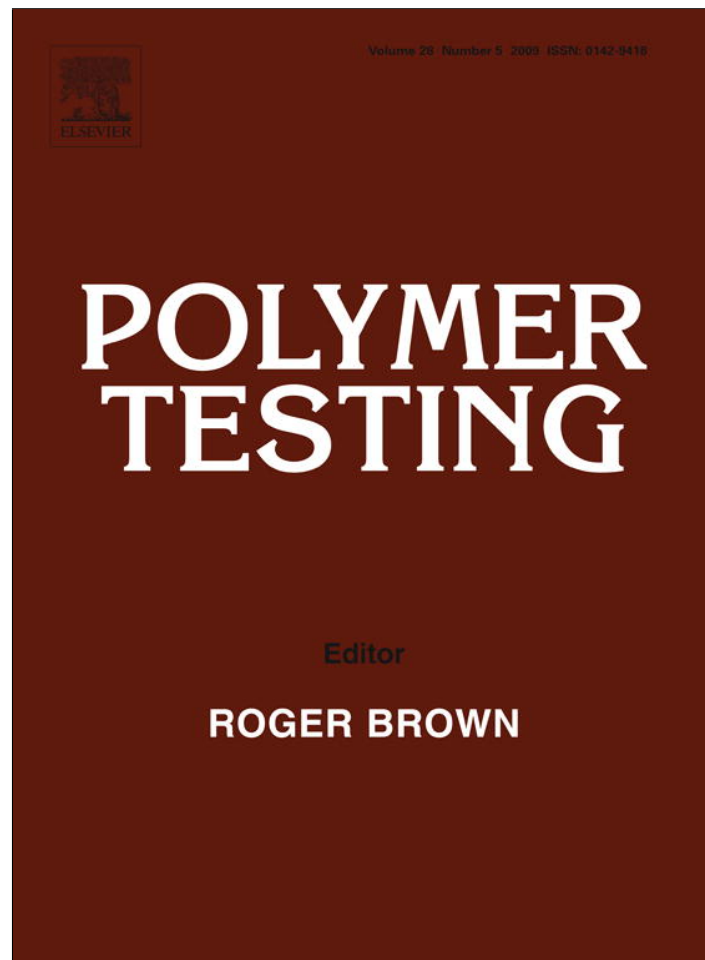


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## Analysis Method

NMR study of styrene-butadiene rubber (SBR) and TiO<sub>2</sub> nanocompositesTatiane M. Arantes<sup>a</sup>, Katyuscya V. Leão<sup>b</sup>, Maria Inês B. Tavares<sup>c</sup>, Antonio Gilberto Ferreira<sup>b</sup>, Elson Longo<sup>d</sup>, Emerson R. Camargo<sup>a,\*</sup><sup>a</sup> LIEC-Laboratório Interdisciplinar de Eletroquímica e Cerâmica, UFSCar-Federal University of São Carlos, Rod.

Washington Luis km 235, CP 676, São Carlos SP, 13565-905, Brazil

<sup>b</sup> Laboratório de Ressonância Magnética Nuclear, UFSCar-Federal University of São Carlos, Rod. Washington Luis km 235, CP 676, São Carlos SP, 13565-905, Brazil<sup>c</sup> IMA/UFRRJ, Center of Technology, Bloco J, Cidade Universitária, Ilha do Fundão, CP 68525, Rio de Janeiro RJ, 21945-970, Brazil<sup>d</sup> LIEC-IQ, Chemistry Institute of Araraquara, Department of Biochemistry and Technological Chemistry, UNESP-São Paulo State University, Rua Francisco Degni, CP 355, Araraquara SP, 14801-907, Brazil

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## ABSTRACT

The chemical behavior of styrene-butadiene rubber (SBR) and of the SBR/TiO<sub>2</sub> and photodegraded SBR/TiO<sub>2</sub> nanocomposites was investigated through nuclear magnetic resonance spectroscopy (NMR) in the solid state with magic angle spinning (MAS). The <sup>13</sup>C cross polarization/magic angle spinning (CP/MAS) routine spectrum allowed us to obtain information on the polymer microstructure and also to evaluate the domain mobilities. The variation contact time and the proton spin-lattice relaxation time in the rotating frame (T<sub>1ρ</sub>H) were determinant factors to evaluate the dynamic molecular motion. The NMR spectrum of the nanocomposites was dislocated 5 ppm to higher chemical shift, indicating the presence of a strong interaction between the polymer chains and the TiO<sub>2</sub> nanoparticles. The VTC experiment showed a rigid domain in the SBR/TiO<sub>2</sub> photodegraded nanocomposite due to cross-linking reactions.

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## 1. Introduction

It is well known that the incorporation of nanofillers, such as silica, modified clays and some oxide nanoparticles, in a polymeric matrix can markedly promote improvements in mechanical and chemical properties of nanocomposites [1–3]. Because of the scientific and commercial importance of these materials, numerous efforts have focused to understand the effect of the nanofillers on the performance of an elastomeric matrix through different analytical techniques, for instance transmission electronic microscopy (TEM), thermal analysis, X-ray scattering (SAXS), mechanical measurements and many others.

Specifically, solid-state nuclear magnetic resonance spectroscopy (NMR) became a powerful technique of probing for structural and dynamic information of elastomeric nanocomposites at molecular level [4]. Solid-state NMR allows easy preparation and direct measurement of samples free of any solvent and offers a variety of techniques to investigate the dynamic molecular interaction process. The instrumental improvements have resulted in solid state spectra with comparable quality to the traditional liquid NMR, and when some techniques are used, such as magic angle spinning (MAS) and cross polarization (CP), the line broadening is reduced and the NMR signal sensitivity increased, making solid-state NMR a powerful tool to obtain information about homogeneity and domain structures during the analysis of polymers, polymer blends, composites and, recently, polymeric nanocomposites [5–10]. Some attempts have recently been made to correlate cross polarization rates to the cross-link density in elastomers. The presence of dynamic physical and permanent chemical

\* Corresponding author. Tel.: +55 16 3351 8090; fax: +55 16 3351 8350.

E-mail addresses: [tatiane@liec.ufscar.br](mailto:tatiane@liec.ufscar.br) (T.M. Arantes), [kvleao@yahoo.com.br](mailto:kvleao@yahoo.com.br) (K.V. Leão), [mibt@ima.ufrrj.br](mailto:mibt@ima.ufrrj.br) (M.I.B. Tavares), [giba\\_04@yahoo.com.br](mailto:giba_04@yahoo.com.br) (A.G. Ferreira), [elson@iq.unesp.br](mailto:elson@iq.unesp.br) (E. Longo), [camargo@ufscar.br](mailto:camargo@ufscar.br) (E.R. Camargo).

cross-links in elastomers leads to a non zero average of the homonuclear and heteronuclear dipolar couplings, resulting in a solid-like NMR relaxation behavior [10].

In this work, we prepared nanocomposites of synthetic titanium oxide nanoparticles and commercial styrene-butadiene rubber (SBR) produced on industrial scale in latex form. The nanoparticles were synthesized by means of a solution route under mild conditions of temperature and pressure, with controlled spherical size, average diameter of 6 nm and sharp size distributions. Nanocomposites films were obtained from the mixture of these nanoparticles and the SBR latex through solvent elimination, resulting in a material with high photocatalytic sensitivity. Solid-state NMR was used to characterize the structural and dynamic behavior, evaluating the domain molecular mobility of the pure elastomer and of the nanocomposites before and after photodegradation.

## 2. Experimental section

All the chemicals used in this work were of analytical grade and were used as received with no further purification. The water used was deionized through a Millipore Elix-3 purification system.

### 2.1. Synthesis

Nanoparticles of titanium oxide were prepared following the method described originally by O'Brien et al. [11]. Titanium (IV) isopropoxide (0.185 mL, Merck-Germany, 97%) was dissolved in diphenylether (30 mL, Merck-Germany, 99.0%) in the presence of oleic acid (Merck-Germany, 99.0%). The alkoxide was added under an inert atmosphere to prevent its premature hydrolysis, and the nominal titanium concentration in this solution was  $0.02 \text{ mol L}^{-1}$ . An aqueous solution of hydrogen peroxide (Sinth-Brazil, 30%) was injected into the system at  $70^\circ\text{C}$  under stirring to promote controlled hydrolysis of the titanium alkoxide ( $\text{H}_2\text{O}_2:\text{Ti} = 8:1$ ). The flasks were kept at  $120^\circ\text{C}$  for 12 h, after which the nanoparticles were isolated by centrifugation, washed with hexane and dried. The nanoparticles were dispersed in water with the addition of  $0.1 \text{ mol L}^{-1}$  of dodecylbenzenesulfonic acid (DBSA), and transferred to the SBR colloidal lattices dispersions. After 1 h of homogenization, the SBR lattices with  $\text{TiO}_2$  nanoparticles were dried using Petri dishes in an air circulation oven at  $50^\circ\text{C}$  for several hours, and then deployed as self-sustained films of nanocomposite.

### 2.2. Photodegradation

Square samples with an area of  $2 \text{ cm}^2$  and a thickness of 0.5 mm were prepared from the nanocomposite films with different amounts of  $\text{TiO}_2$  nanoparticles. These samples and one control sample (without nanoparticles) were placed in a dark box and set at distance of 10 cm from the UV source to perform the photodegradation reactions. The radiation used in this experiment was obtained using a medium pressure mercury vapor lamp (OSRAM – HQL 400) without the protection bulb.

## 2.3. Characterization

Solid-state NMR spectra were obtained using a VARIAN Unity 400 spectrometer, operating at 100.2 MHz for  $^{13}\text{C}$ . All of the NMR experiments were done with the probe at ambient temperature and were performed using gated high decoupling. A zirconium oxide rotor of 7 mm diameter was used to acquire the NMR spectra at rates of 6 kHz. The  $^{13}\text{C}$  NMR spectra were carried out in the magic angle spinning (MAS) with short recycle delay (0.3 s) between  $90^\circ$  pulses. The recycle delay was 2 s in the cross-polarization mode with magic angle spinning (CPMAS). Proton  $T_{1\rho\text{H}}$  values were determined from the intensity decay of  $^{13}\text{C}$  peaks, varying the spin-locking from 200 to  $8000 \mu\text{s}$  at a constant contact time.

## 3. Results and discussion

Recently, O'Brien et al. [11] proposed a sol-gel technique to prepare oxide nanoparticles from the hydrolysis of an appropriate alkoxide. In our case, we used titanium (IV) isopropoxide diluted in diphenylether. Unlike other forms of synthesis in organic media, where the solvent acts also as a reactant, in this route, diphenylether is only the non polar medium for the formation of inverse micelles of oleic acid. The role played by oleic acid is remarkable, since the crystallization occurs inside the inverse micelle. It is therefore crucial to use the correct amount of oleic acid to ensure precise control of the shape and phase purity of the final compounds. Several experiments were done using different mole ratio of oleic acid and titanium, but pure anatase was only crystallized when the correct mole ratio of 3:1 was used, as observed by the X-ray pattern of Fig. 1, where all of the peaks were attributed to the anatase phase. Larger and smaller amounts of oleic acid resulted in a mixture of rutile and anatase, which shows some dependence between the crystalline phase and the particle size, benefiting the anatase phase for small crystals up to 30 nm [12]. It is important also to note that the polar core of the inverse micelles contains water from the hydrogen

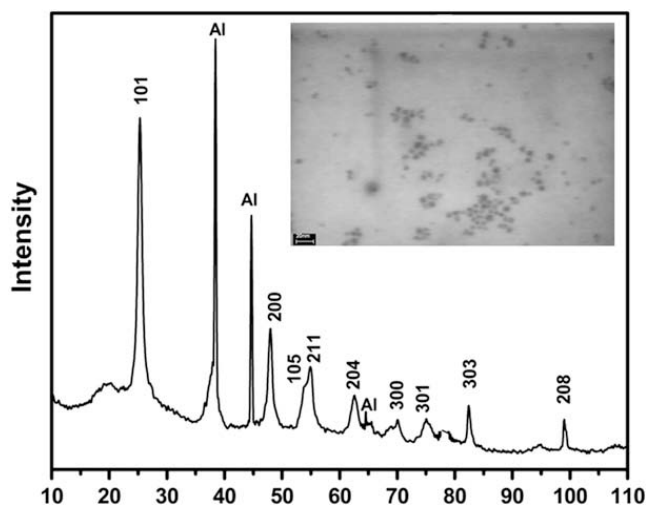


Fig. 1. XRD pattern of  $\text{TiO}_2$  nanoparticles with oleic acid as surfactant in the ratio of 1Ti:3OLA. Inset shows the FEG-STEM micrograph of  $\text{TiO}_2$  nanoparticles. Al indicates the aluminum substrate.

peroxide, pushing the system to form nanoparticles with smaller volumes than those found inside the micelles [13].

These particles were also characterized by scanning/transmission electron microscopy (FEG-STEM) to check the morphology of the particles (the inset in Fig. 1). This image shows almost uniform spherical nanoparticles with an average size of 7 nm, located at approximately the same distance from each other. This uniform spatial arrangement of nanoparticles indicates that their surfaces are coated by oleic acid, forming a hydrophobic layer that stabilizes the colloidal particles in the non polar medium, but resulting in water-insoluble particles. To obtain stable aqueous colloidal dispersions, the hydrophilic nature of the nanoparticles had to be modified. Aqueous solutions of dodecylbenzenesulfonic acid were prepared, to which the TiO<sub>2</sub> nanoparticles were added, and the system was stirred for 1 h at room temperature, resulting in stable aqueous colloidal dispersions of TiO<sub>2</sub> nanoparticles.

There are several methods to prepare nanocomposites, for instance *in situ* polymerization, melting routes, mechanical extrusion and solution processing. [2] In this work, the SBR/TiO<sub>2</sub> nanocomposites were prepared by the colloidal route. Following this procedure, colloidal dispersions of hydrophilic TiO<sub>2</sub> modified with DBSA were added to the commercial aqueous dispersions of SBR lattices and homogenized at room temperature. Self-sustained nanocomposite films were prepared easily through solvent evaporation. During this stage, the SBR colloids agglutinated and the TiO<sub>2</sub> nanoparticles were trapped in this process, maintaining their original homogeneity, and

resulting in SBR nanocomposite films containing 0.2% (in mass) of TiO<sub>2</sub> nanoparticles.

Pure SBR elastomer, SBR/TiO<sub>2</sub> nanocomposite and SBR/TiO<sub>2</sub> photodegraded nanocomposite were analyzed by solid-state <sup>13</sup>C NMR, using MAS with the high power proton decoupling technique, which was carried out to observe the mobile region, using a short delay between 90° pulses. The spectra obtained are shown in Fig. 2 and the chemical shifts that were assigned on the basis of earlier literature [9,14–16] are shown in Table 1.

Despite the fact that the spectrum of the non degraded SBR/TiO<sub>2</sub> nanocomposite is identical to the pure SBR elastomer as regards the number, shape and relative intensities of the peaks, it is possible to observe that the nanocomposite spectrum is dislocated 5 ppm to higher chemical shift, possibly due to the interaction of the TiO<sub>2</sub> nanoparticles on the interaction between polymer chains. This effect is a good inference of the strong action of nanoparticles on the organization of the chains in nanocomposites. It is also possible to note a broadening of NMR signals after the photodegradation and the absence of the characteristic assignments of butadiene, indicating that the butadienic chain was effectively photodegraded.

Several groups have studied the photocatalyzed degradation of polymers that contain polybutadiene groups, such as butadiene rubber (BR) [18], nitrile rubber (NBR) [17], acrylonitrile-butadiene-styrene (ABS) [18,19] and styrene-butadiene rubber (SBR) [20,21]. It has been suggested that degradation is mainly controlled by the reactivity of the 1,2-butadiene and of the *cis* and *trans*-1,4-butadiene

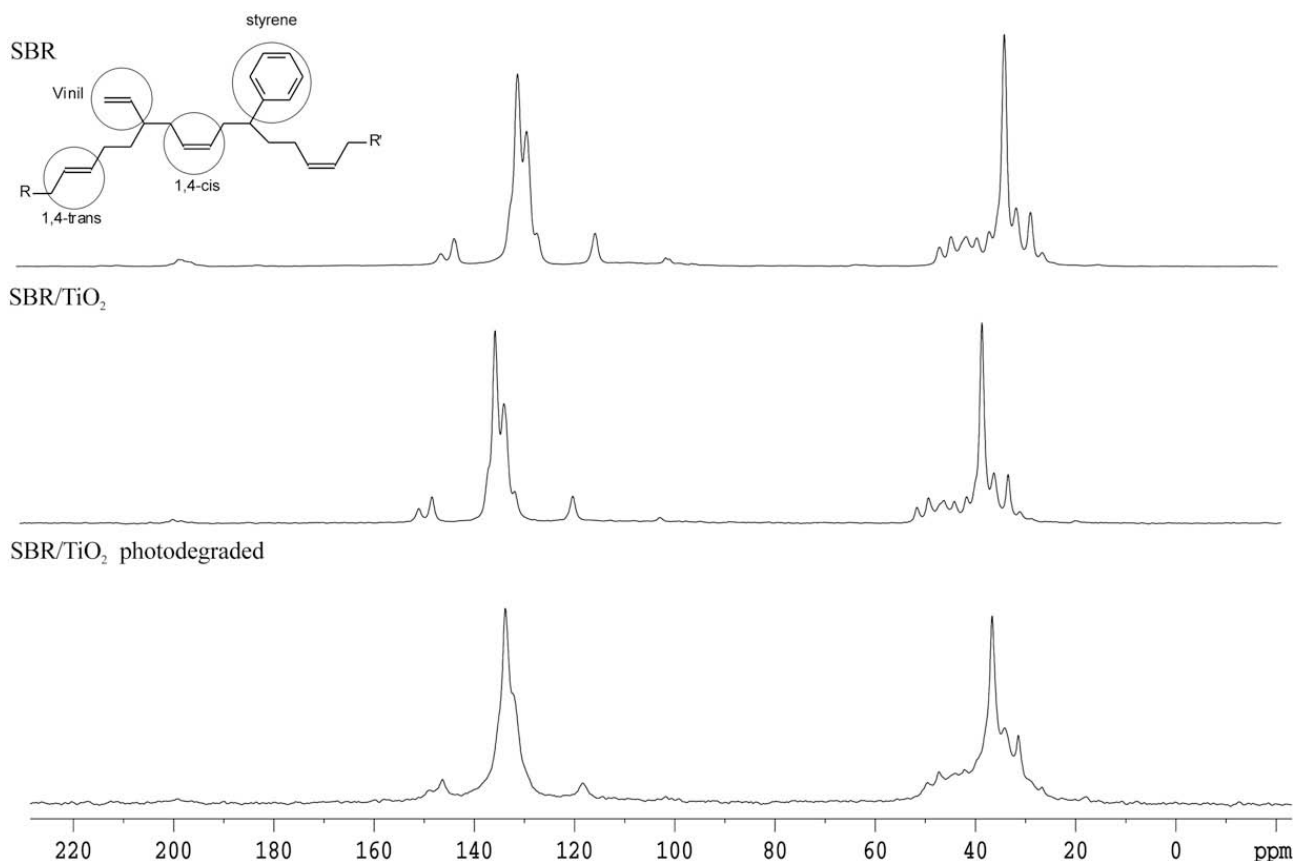


Fig. 2. Solid-state <sup>13</sup>C NMR MAS spectra: (a) SBR; (b) nanocomposite SBR/TiO<sub>2</sub> 0.2% and (c) nanocomposite SBR/TiO<sub>2</sub> 0.2% photodegraded.

**Table 1**  
 $^{13}\text{C}$  NMR chemical shifts ( $\delta = \text{ppm}$ ) of SBR and SBR/TiO<sub>2</sub> nanocomposites.

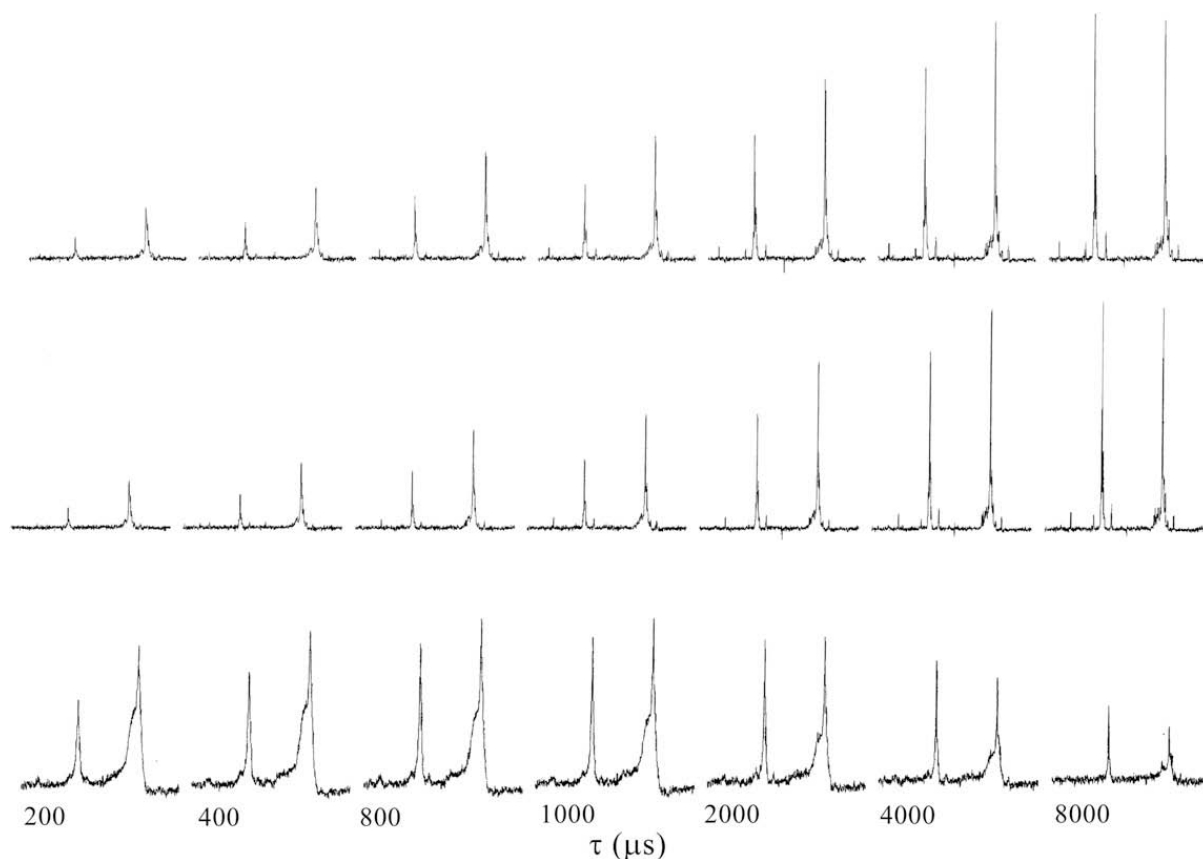
Structure	SBR $\delta/\text{ppm}$	SBR/TiO <sub>2</sub> $\delta/\text{ppm}$
C <sub>1</sub> aromatic	143.8	148.9
CH=CH vinyl	141.2	146.3
C <sub>2</sub> and C <sub>4</sub> aromatic	130.0	135.1
C <sub>3</sub> and C <sub>3</sub> (S) and CH=CH 1,4 (T)	128.6	133.8
CH=CH 1,4 (C)	126.7	132.1
C <sub>4</sub> aromatic	124.8	129.8
=CH <sub>2</sub> vinyl	113.1	118.2
CH <sub>2</sub> styrene	44.3	49.5
CH <sub>2</sub> styrene	41.9	47.2
C <sub>z</sub> styrene	39.0	44.1
CH <sub>2</sub> 1,2 vinyl	36.8	42.1
CH <sub>2</sub> 1,4 trans	34.5	39.6
CH <sub>2</sub> 1,4 cis	32.8	37.8
CH <sub>2</sub> 1,2 vinyl	31.4	36.5
CH <sub>2</sub> 1,4 cis	28.9	34.0
CH <sub>2</sub> 1,2 trans	26.2	31.3
CH <sub>2</sub> 1,2 cis	23.8	28.1

Peaks with chemical shifts in 99.0 and 98.2 appear due to impurities present in the SBR latex.

isomers. The broadening observed in the NMR spectrum indicates that the molecular mobility of the polymer chains is reduced after photodegradation. This is mainly due to the fact that the resonance line width is related to the segmental polymer motion. If the molecule is free to move in any direction, then the spectrum line width is narrow. On the other hand, if the motion is restricted, then the line width increases. In terms of rubber degradation processes,

it seems to be consistent with the formation of extra cross-links restricting the motion of molecules, since the chains lose their ability to move as individual polymer chains [22].

Analyzing the pure SBR and the SBR/TiO<sub>2</sub> nanocomposites spectra according to variable contact-time (VCT) experiments (Fig. 3), two domains with very different molecular mobilities were encountered. The signal distribution profile shows clearly a large and flexible domain for the pure SBR and SBR/TiO<sub>2</sub> nanocomposite samples, but a rigid domain for the SBR/TiO<sub>2</sub> photodegraded nanocomposite. According to Coelho et al. [23], the intensity of the NMR signals during the cross-polarization experiment depends on the rate of cross-polarization from the  $^1\text{H}$  nuclei to near neighbor  $^{13}\text{C}$  nuclei, which makes it possible to determine the proton spin-lattice relaxation time in the rotating frame ( $T_{1\rho\text{H}}$ ). In an atactic and amorphous flexible polymer, such as polybutadiene rubber, the molecular motion reduces the interaction of the dipole moments and, consequently, the cross-polarization is a slow process [23]. Spectra a and b (Fig. 3) show peaks located at long contact times, in agreement with rubbery materials. On the other hand, the spectrum c of SBR/TiO<sub>2</sub> photodegraded nanocomposite shows a rigid domain in the VTC decay profile. It is well known that polymer become more rigid after photodegradation. Considering that some cross-linking reactions occur between the polymer chains during the degradation process, the material becomes more rigid and less soluble in organic solvents. These reactions occur



**Fig. 3.**  $^{13}\text{C}$  NMR CP/MAS spectra with variable contact-time experiment (VCT): (a) SBR, (b) SBR/TiO<sub>2</sub> nanocomposite and (c) SBR/TiO<sub>2</sub> photodegraded nanocomposite.

**Table 2**

Proton spin-lattice relaxation time in the rotating frame values for all resolved  $^{13}\text{C}$  of SBR, SBR/TiO<sub>2</sub> nanocomposite, SBR/TiO<sub>2</sub> photodegraded nanocomposite.

d (ppm)	SBR T <sub>1ρ</sub> H (ms)	SBR/TiO <sub>2</sub> T <sub>1ρ</sub> H (ms)	SBR/TiO <sub>2</sub> Photodegraded T <sub>1ρ</sub> H (ms)
38	13.5	–	–
36	10.3	–	2.2
31	25.7	–	–
29	43.2	393	–
133	–	–	7.3

particularly on the chains containing  $\alpha,\beta$ -unsaturated carbonyl [20,21]. The values of proton T<sub>1ρ</sub>H for the resolved carbons were calculated and listed in Table 2.

The non-uniformity in the values of T<sub>1ρ</sub>H shows that the system is heterogeneous and that there are structural changes. The proton T<sub>1ρ</sub>H evaluates the changes in the microstructure and the molecular mobility in polymer blends. This parameter also permits verification of the homogeneity in the polymer systems, as it is sensitive to the spatial proximity of chains. Generally speaking, for a compatible blend, just one value of this parameter is found. More than one value is an indication that, at least, two domains with distinct mobilities were found [24]. This statement was verified for the systems analyzed.

#### 4. Conclusions

The colloidal route is a suitable method to prepare nanocomposites of SBR and synthetic anatase nanoparticles. It was observed that the spectrum of the non degraded SBR/TiO<sub>2</sub> nanocomposite is identical to the pure SBR elastomer regarding the number, shape and relative intensities of the peaks, but it is dislocated 5 ppm to higher chemical shift, indicating the presence of a strong interaction between the polymer chains and the TiO<sub>2</sub> nanoparticles. After the photodegradation, characteristic assignments of butadiene were not observed, indicating that the butadienic chain has been degraded. In the VTC experiment, the signal distribution profile shows clearly a large flexible domain for SBR and SBR/TiO<sub>2</sub> nanocomposite and a rigid domain in the SBR/TiO<sub>2</sub> photodegraded nanocomposite due to cross-linking reactions.

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