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RELAXATION OF HYDROGEN TO EVALUATE THE ORGANIZATIONAL STRUCTURE OF PC/TiO_2 NANOCOMPOSITES

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ABSTRACT

Time-domain nuclear magnetic resonance (TD-NMR) was used to characterize blends of polycarbonate and titanium dioxide from proton spin-lattice relaxation times, which allows analyzing the influence of nanoparticles incorporation in the polymer structure. Differences in longitudinal relaxation time (T_1H) and distribution curves of the relaxation times were related to alterations in the rigidity, and consequently the homogeneity of the materials. The modifications in the pattern of domain curves indicated the influence of each processing temperature. The results demonstrated that it is possible to alter the properties of the polycarbonate by increasing titanium oxide concentration, which tends to cause its agglomeration while processing temperature directly affects the structure of the obtained materials.

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INTRODUCTION

Polycarbonates (PCs) are linear polyesters produced by polycondensation of carbonic acid and aromatic or aliphatic dihydroxylated compounds (Merat *et al.,* 2011). These polymers are important materials for engineering applications due to their good mechanical and physical properties, such as impact resistance, thermal resistance, dimensional stability, transparency (90%) and rigidity. However, they also have characteristics that limit their use in some applications, such as low resistance to radiation, hydrolysis and solvents (Merat *et al.,* 2011; Chimanowsky *et al.,* 2014). PCs are amorphous, hygroscopic, odorless and tasteless polymers. The presence of benzene groups in the chain of PCs gives them molecular stiffness, high melting temperature (Tm=275 °C) and high glass transition temperature (Tg=150 °C) (Chimanowsky *et al.,* 2015).

The inclusion of inorganic nanoparticles in organic polymer matrices has attracted a good deal of scientific attention. The formulation of organic/inorganic nanocomposites offers an effective way to improve the physical and mechanical properties of conventional polymers, such as chemical resistance. This can be achieved using very low filler concentrations when compared to microparticle loads (Esthappan *et al.,* 2012). In recent decades, three distinct TiO_2 allotropes (rutile, anatase and brookite) have been extensively studied due to their attractive electrical, magnetic, catalytic and electrochemical properties (Man *et al.,* 2012; Rodrigues *et al.,* 2012). Nanocomposites properties rely not only on the features of their individual components, but also on the way in which they interact polymer-filler interface (Paul *et al.,* 2008). With the increasing interest in the use of polymeric nanocomposites, the evaluation of their compatibility with other substances, their dispersed phase properties, homogeneity in dispersion and microstructure are becoming every day more important (Paul *et al.,* 2008). Low-field nuclear magnetic resonance (LF-NMR) spectroscopy has been used to develop methods to measure nuclear relaxation to characterize polymeric materials

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(Paul *et al.,* 2008; AO *et al.,* 2014; Bovey and Mirau, 1996; Komoroski, 1986; McBrierty and Packer, 2006; Almeida *et al.,* 2012). In fact, because of the sensitivity to molecular segments mobility, experiments involving NMR are virtually the only tool to analyze the different states of order that coexist in semicrystalline polymers, since this technique is extremely sensitive to molecular mobility (AO *et al.,* 2014; Bovey and Mirau, 1996; Komoroski, 1986; McBrierty and Packer, 2006; Almeida *et al.,* 2012). The signals obtained generally indicate an overlap of at least three components, associated with protons in crystallites, in regions in the molten state and in amorphous regions with reduced mobility (AO *et al.,* 2014). It was previously demonstrated that time-domain NMR can be a valuable tool for polymer characterization, by revealing their structure and identifying potentially defective blocks (Bovey and Mirau, 1996; Komoroski, 1986; McBrierty and Packer, 2006; Almeida *et al.,* 2012). Taking into consideration the advantages of LF-NMR, this study evaluates the quality of dispersion and distribution of TiO_2 nanoparticles in PC and its influence on the resultant composite domains by means of time-domain ^1H NMR.

MATERIALS AND METHODS

The PC sample (bisphenol A) was supplied by Polycarbonate S.A. Indústria e Comércio (Camaçarí, Bahia, Brazil), with molar weight (Mw) of 44,460 g/mol. The TiO_2 was supplied by Degussa-Evonik, São Paulo, Brasil, in rutile form. Both the PC and TiO_2 were dried in an oven at 50 °C for approximately 48 hours. The polycarbonate pellets were ground in a knife mill and the resulting powder was mixed with the previously dried titanium dioxide in concentrations of 1%, 3% and 5% by weight of TiO_2. Both the physical blend of PC/TiO_2 and pure PC powder were used to feed the mixing chamber of a Haake rheometer. The samples were processed at three temperatures: one near the Tm of the bisphenol-A PC (270 ºC), and the others were 240 and 300 ºC. When heated to 240 ºC, the rheometer was adjusted to operate at 30 rpm, while at 270 ºC it was adjusted to 60 rpm and at 300 ºC to 90 rpm. The purpose of these settings was to assure that the degree of viscosity indicated by the rheometer, during the mixing process, was the same. The samples were mixed for 8 minutes, after which the material was removed and allowed to cool naturally between two metal plates. As final step, the samples were pressed at 6 tons in a hydraulic press at 180 °C, with the aid of kapton tape. The pressure was applied for 10-minute periods with reliefs every 2 minutes for degassing. The films obtained were used along the different tests. The relaxation times of the hydrogen nucleus employing time-domain NMR were measured at 0.54 T in a Maran Ultra spectrometer (Oxford Instruments) with an 18 mm probe, operating at 23.4 MHz (for hydrogen). The spin-lattice relaxation times of hydrogen (T_1H) were measured at 28 °C, with receiver gain of 2%. The tau range (τ) used was 0.1 – 5000 milliseconds (ms) with 4 scans (NS) each. The T_1 values and their relative intensities were obtained by fitting the exponential data with the support of the WINFIT program. The exponential fits were plotted on a graph of amplitude as a function of relaxation time, using the WINDXP software.

RESULTS AND DISCUSSION

Tables 1 to 3 show the values of relaxation times determined for each sample. Figures 1 to 3 exhibit the distribution of relaxation times domains of hydrogen (T_1H) for the PC systems processed at temperatures of 240 ºC, 270 º and 300 ºC, respectively. In the systems processed at 240 °C, the addition of TiO_2 did not modify the T_1H times in the more rigid region at any of the concentrations studied.

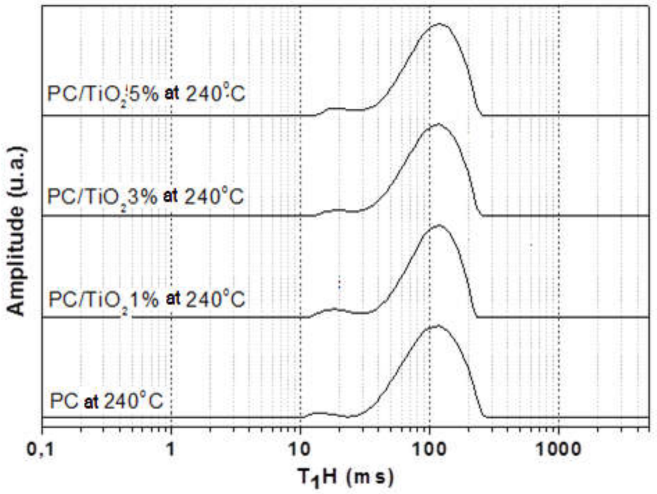

Figure 1. Distribution of the domains curves (spectrum of relaxation) for the PC/TiO_2 systems processed at 240 ºC.

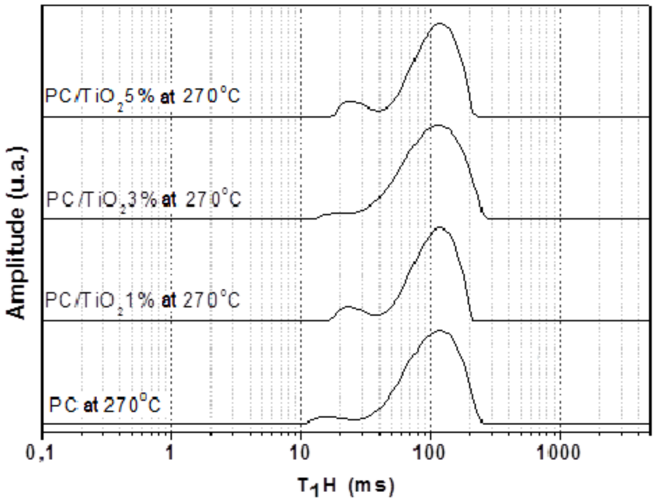

Figure 2. Distribution of the domains curves (spectrum of relaxation) for the PC/TiO_2 systems processed at 270 ºC

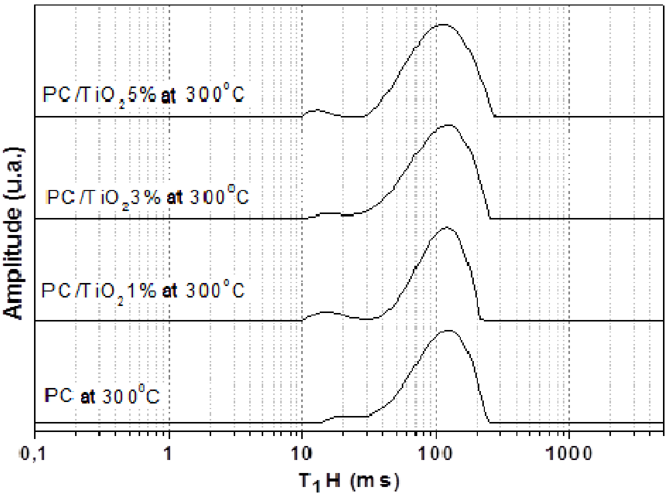

Figure 3. Distribution of the domains curves (spectrum of relaxation) for the PC/TiO_2 systems processed at 300 ºC.

Table 1. Values of relaxation times for the PC/TiO_2 systems processed at 240 °C, for PC and the composites with 1, 3 and 5 % of particles

Sample		Relaxation Time
$T_{1,1}H$	$T_{1,2}H$	
PC/TiO_2 1%	20	118
PC/TiO_2 3%	20	118
PC/TiO_2 5%	18	118
PC	14	118

Table 2. Values of relaxation times for the PC/TiO_2 systems processed at 270 °C, for PC and the composites with 1, 3 and 5 % of particles

Sample	Relaxation Time	
	$T_{1,1}H$	$T_{1,2}H$
PC/TiO_2 1%	23	118
PC/TiO_2 3%	18	118
PC/TiO_2 5%	23	118
PC	15	118

Table 3. Values of relaxation times for the PC/TiO_2 systems processed at 300 °C, for PC and the composites with 1, 3 and 5 % of particles

Sample	Relaxation Time	
	$T_{1,1}H$	$T_{1,2}H$
PC/TiO_2 1%	13	118
PC/TiO_2 3%	15	118
PC/TiO_2 5%	15	118
PC	20	118

However, it slightly increased the rigidity in the population with highest mobility, which shifted from 14 to 20 ms. Besides this, the concentration of 1% led to the formation of a more homogeneous matrix, with narrower main domain, at 118 ms. That behavior indicates that the lowest processing temperature, below the Tm of PC, hampered the dispersion of the nanoparticles, an effect that was less prejudicial at the lowest concentration (1%), leading to a more homogeneous matrix. On the other hand, despite the lower processing temperature, the increase of TiO_2 concentrations conferred greater rigidity without improving the homogeneity of the more rigid phase. This can be explained by the relatively high quantities of TiO_2 nanoparticles, which hindered the dispersion and distribution of these particles in the PC matrix, contributing to competition between protection and degradation. For nanocomposites processed at 270 °C, it was seen that the higher processing temperature favored more mobile fraction in comparison to 240 °C, shifting the T_1H value from 15 ms to 23 ms. For the systems containing nanoparticles concentrations of 1% and 5%, the T_1H values suggest that microstructure of the PC was better organized, presenting peak base narrowing of the more rigid ^1H nuclei population.

The sample containing 3 % of nanoparticles – possibly for reasons related to processing or mixture in the rheometer – showed adverse T_1H relaxation time profile which includes wide domains and reduction of T_1H values of the most mobile phase, characterizing thus a more heterogeneous and brittle material. In other words, the higher processing temperature enabled better nanoparticles dispersion for the samples with 1 % and 5 % TiO_2. When processing temperature was 300 °C, the rigidity of the pure PC became higher, with the T_1H value of the mobile phase shifting to 20 ms. However, the addition of TiO_2 at this temperature resulted in lower T_1H values and broader mobility domains for the nanocomposites, suggesting that the polymer could be starting a degradation process, aided by the presence of nanoparticles. Therefore, the system was more heterogeneous, with the effects being more pronounced at the nanoparticle concentration of 5%, including an increase of mobility of the more rigid populations. The relaxation curves were used to extract the molecular mobility of domains/segments of T_1H values for each sample, through inverse Laplace transform. All the materials presented two domains: one in the region of 10 to 30 ms and the other located at 118 ms. Each domain represents a region of the system where the chains or segments assume a molecular organization, which involves molecular movements from collective groups. The molecular segments or domains that presents shorter times correspond to polymer chains with greater mobility, due to the movement of small groups or collective segments, in this case, water. Domains with long relaxation values indicate more rigid molecular organization on regions that are more tightly packed or have greater molecular movement restriction due to the lower collective segment's motions impediment. The width of the peak base of each domain is related to the degree of homogeneity of hydrogen nuclei population. Narrower peak bases point to a more homogeneous or organized region, while broader bases suggest greater heterogeneity, i.e., a larger number of different organizations within that population of ^1H, due to the dispersion and distribution of the nanoparticles in the polymer matrix promoted by the method used, which can provide multiple intermolecular interactions. The area of each domain is directly proportional to the number of ^1H nuclei that compose that region of the polymer matrix. For all the systems, the smallest domain contained about 10% of ^1H nuclei population and the largest about 90% of the ^1H nuclei population.

Conclusion

Nuclear relaxation analysis was used to study the quality of dispersion and distribution of TiO_2 nanoparticles and the effects of both processing time and temperatures higher than Tm of polymer matrix after nanoparticle incorporation. The systems containing 1% TiO_2 showed greater homogeneity regarding the ^1H nuclei. The best processing temperature was 270 °C, which showed better nanoparticles dispersion into the polymer matrix as well as avoiding polymer degradation that can come across when processing temperatures are higher than Tm. The processing at 240 °C produced less homogenous systems, presenting better results for the lowest titanium dioxide concentration, mainly since mixture occurred below the Tm of PC. Probable polymer degradation was observed for the 5% PC/TiO_2 system processed at 300 °C. The 1% and 5% PC/TiO_2 systems processed at 270 °C presented the best results, due respectively to the better dispersion of the nanoparticles in lower concentrations and the effect of the larger quantity of oxide, even though the dispersion was not as efficient.

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