

The Evaluation of Polycarbonate Films by Proton Relaxation Time

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Abstract: Polycarbonates are polymers of high industrial interest, which can be mainly attributed to their mechanical properties, such as good impact resistance. Thus, investigating their structures plays a fundamental part in the development of new applications; the study of molecular dynamic behavior can be done as a function of polycarbonates modifications. Generally, cast films from diluted solutions, pressed films, and crystallinity induction are sources used to evaluate the responses to the changes in the dynamic behavior of these polymers. In this work, we have prepared polycarbonate films by solution casting, using crystallinity inducer solvent, and by thermal press. The evaluation of the changes in the polycarbonate films was carried out by low field nuclear magnetic resonance spectroscopy by determining proton spin-lattice (T_1) and spin-spin relaxation time (T_2) in two temperatures (25°C and 35°C). The results were compared to those of a commercial polycarbonate. The relaxation studies revealed useful information on the behavior of polycarbonates.

Resumo: Os policarbonatos são polímeros de alto interesse industrial, o que é normalmente atribuído às suas ótimas propriedades mecânicas, tal como alta propriedade de impacto. Desse modo, à investigação de sua estrutura química e microestrutura constitui uma parte fundamental no desenvolvimento de novas aplicações; o estudo da dinâmica molecular pode ser realizado como função das modificações sofridas por este polímero durante seus processamentos. Geralmente, filmes vazados a partir de soluções, filmes obtidos por prensagem térmica e por indução de cristalinidade são fontes usadas para avaliar as respostas das mudanças do comportamento dinâmico destes polímeros. Neste trabalho nós preparamos filmes de policarbonatos via solução, usando solvente indutor de cristalinidade e filmes obtidos por prensagem térmica. A avaliação das mudanças na dinâmica molecular dos filmes obtidos foi realizada por meio de um espectrômetro de RMN de baixo campo para determinação dos tempos de relaxação spin-rede e spin-spin em duas temperaturas 25 ° e 35 °C. Os resultados obtidos foram comparados com os dos polímeros comerciais. Os estudos de relaxação revelaram informações importantes sobre o comportamento dos policarbonatos estudados.

Introduction

The replacement of conventional materials for polymers is an attempt to reduce manufacture costs and benefit society, improving its quality of life. These factors play a major role in the development of new polymeric materials. With the aim to respond to these demands, research has been carried out to change current polymer structures, using copolymers and crystallinity induction in

amorphous materials. The major goal is to increase the polymer potential applicability. Polycarbonates are one class of polymers that has attracted considerable attention, particularly because of their lightweight and high-performance.¹⁻³ This material is commonly used in automobiles, cell phones, computers, CDs, DVDs, to mention just a few of its applications.⁴ The most commonly used polycarbonates are obtained by the reaction of bisphenol A with phosphine (Figure 1).

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Polycarbonate pellets can be transformed into the desired shape for its intended application by melting it and forcing it under pressure into a mould. This polymer is amorphous due to the rigidity of the main chain. These properties result from the presence of aromatic rings, which decreases molecular mobility. Low field NMR has been used for polymers characterization by studying molecular mobility by means of the determination of nuclear relaxation time constant.^{1,2} Two processes of relaxation occur in parallel, one is spin-lattice or longitudinal with time constant T_1 , showing enthalpy characteristic; The other one occurs by energy changes between spins, called spin-spin or transversal, which is more entropic and has a time constant T_2 .

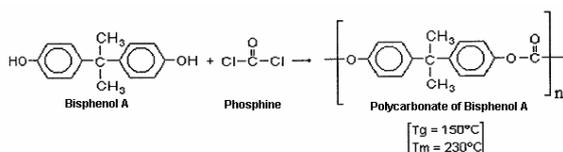


Figure 1. Route for preparation of Polycarbonate of Bisphenol A

Relaxation mechanism is related to internal and global molecular structure. A system will be homogenous when only one value of T_1 is found and heterogeneous when more than one is found. T_1 values can be evaluated considering structural organization and lower flexibility. This value of this parameter (T_1) is much higher than those of T_2 .⁵⁻⁷ T_2 is applied to study domains with different mobilities of polymeric systems, providing information on compatibility, molecule structure and interactions.

Experimental

The solvent used for crystallinity induction

was 1,1 2,2 tetrachloroethylene (TCE), and solutions with 30% w/v (PC/TCE) were prepared at room temperature. After complete polymer solubilization (four days) the casting film was kept for one week in a desiccator. Afterwards, the solvent was completely eliminated in a vacuum oven at room temperature. The thermal pressed film was obtained by melting the polymer mass applying an 8 ton, at 260°C for 15 minutes. The low field measurements were carried out on a Resonance MARAN Ultra 23 NMR spectrometer. Spin-lattice relaxation time was measured using an inversion-recovery pulse sequence ($180^\circ - \tau - 90^\circ$), with a range of τ varying from 0.1 a 5,000 ms and recycle delay of 5s. Spin-spin determinations were performed by using a spin-echo pulse sequence (CPMG) ($90^\circ - \tau - 180^\circ$), with τ value of 27 ms and 5s of recycle delay. Both relaxation times were determined at 25°C and 35°C.⁸

Results and Discussion

Table 1 exhibits the proton relaxation parameters for PC films. Two different mobility domains for the polycarbonate pellet were detected. Although the material was amorphous, it formed clusters with different molecular mobilities. After thermal press in the melting state, three distinct domains at 25°C, were found, which were associated to a higher molecular restriction. However, at 35°C only two domains were detected, which can be explained by the increase in molecular mobility. When crystallinity was induced, two domains were detected at 25°C, while three others were detected at 35°C. These findings can be attributed to the increase of mobility,

leading to organizational rearrangements. In accordance with the spin-lattice relaxation data, it was observed that, for the polycarbonate pellet, the temperature used in the thermal press was not high enough to destroy the thermal history of the polymer. Table 1 exhibits the proton relaxation parameters for PC films.

Table 1. Proton relaxation parameters for PC films.

Sample	T_1 (ms)		T_2 (ms)	
	25°C	35°C	25°C	35°C
Pellet	---	---	0.04	2
	33	41	---	7
	116	134	---	50
Thermal pressed	26	34	0.1	0.2
	92	129	0.4	151
	168	---	---	196
Induced film	41	82	7	1.4
	168	175	73	16
	---	229	269	80
	---	---	432	95

Figures 2 (a) and (b) show T_1 timing relaxation distribution for the polycarbonate after the samples have been thermally pressed at 25°C and 35°C respectively.

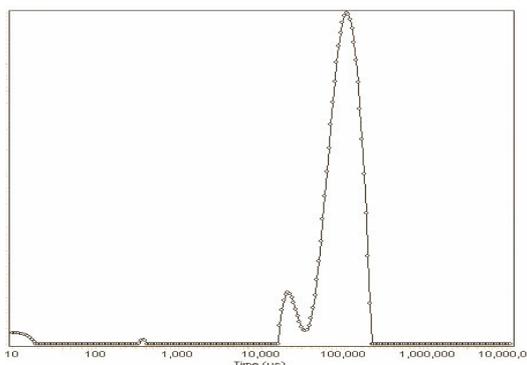


Figure 2(a). T_1 timing relaxation distribution (time μ s/relative amplitude) for the polycarbonate after it has been thermal pressed at 25°C.

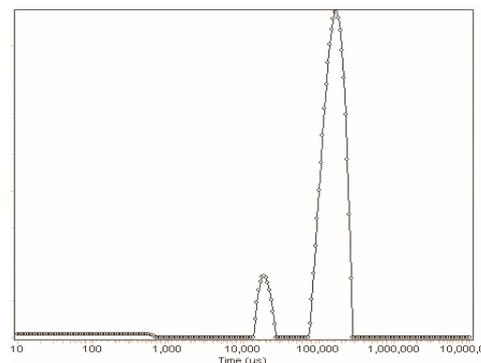


Figure 2(b). T_1 timing relaxation distribution (time μ s / relative amplitude) for the polycarbonate after it has been thermally pressed at 35°C.

The T_2 values show that important changes occurred in structural reorganization. These changes can be associated with the treatment to which the polymer was submitted. It is important to highlight that the domains proportional intensities show different values, such as T_2 intensity for the film after thermal press, as can be seen in the domains distribution curve (Figure 3). T_2 behavior for the films after crystallinity induction showed that an increase of 10°C in the temperature promoted a molecular reorganization, generating a material with a higher hardness, since T_2 values in this temperature were smaller than those at 25°C.

T_2 distribution curve shows only an extremely large signal (Figure 3) at 25°C, while three domains of different mobilities were observed at 35°C. The smaller domain intensity was extremely high, as compared to the others, indicating that this domain controls the relaxation material process. The 0.2 ms relaxation time was attributed to the other domains formed by the amorphous phase homogeneity. The two higher relaxation values can be attributed to the other domains of higher mobility, which can be formed by

smaller length chains.

In Figure 3(a), the distribution profile of the material domains after thermal press shows that the material is completely amorphous.

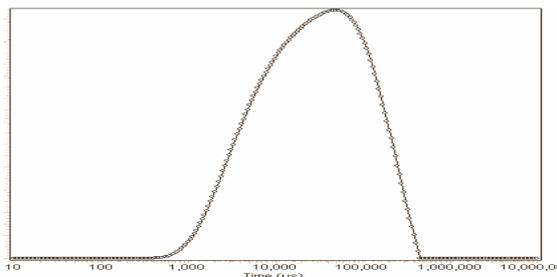


Figure 3(a). T_2 CPMG distribution (time μs /relative amplitude) profile of the material domains after thermal press at 25°C.

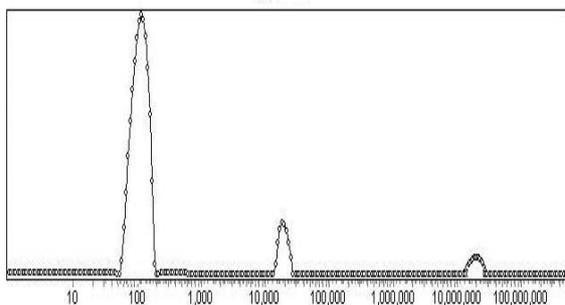


Figure 3(b). T_2 CPMG distribution (time μs /relative amplitude) profile of the material domains after thermal press at 35°C.

The observed changes for the polycarbonate after the treatments employed can be accounted for structural reorganization by quenching and crystallinity induction by solvent action. As a result, T_2 measurements for all the systems reinforce the behavior observed in T_1 .

Conclusion

Relaxation studies provide valuable information on the behavior of polymeric materials. Nuclear relaxation timing

determinations (T_1 and T_2) obtained by low field NMR were precise for evaluating the changes caused by the two treatments applied to the polycarbonate. Also, this technique revealed that the structural and morphological reorganizations observed were associated with the increase of the amorphous phase and the induction of crystallinity in the polycarbonate. Low field NMR showed to be a rapid, efficient and precise technique for such analysis. It can also replace other commonly used techniques for these measurements. It is worth stressing that the analyses were carried out on the material in the natural form, without the necessity of previous treatment.

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