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ORIGINAL PAPER

Study on bisphenol-A polycarbonates samples crystallized by acetone vapor induction

Flavia L. B. Omena de Oliveira · Marcia C. A. Moreira Leite · Lessandra O. Couto · Thiago R. Correia

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Abstract Bisphenol-A polycarbonate (PC) is an important amorphous engineering polymer, which can have its crystallinity induced by special environmental conditions. Such crystallization can alter PC properties leading to flaws during its use or to new applications. Cast film samples of PC, prepared from chloroform solutions, were submitted to acetone vapor and characterized by polarized light microscopy (PLM), differential scanning calorimetry (DSC) and Fourier transform infrared spectroscopy (FTIR). PLM showed that the PC crystalline structure was presented as spherulites of different sizes. DSC analysis exhibited a multiple melting behavior for the crystalline structure. FTIR has presented bands shifting and intensity decrease, compared to the samples before treatment. Compression molded samples were characterized by scanning electron microscopy (SEM), DSC and mechanical properties tests. For those samples, DSC also showed the presence of a crystalline phase, with a little increase on surface rugosity observed through SEM. Stress–strain tests presented a decrease on samples performance after acetone exposure.

Keywords Acetone vapor · Crystallinity induction · Bisphenol-A polycarbonate

Introduction

Bisphenol-A polycarbonate (PC) is the most studied and commercialized among the various PC grades. PC is an amorphous engineering polymer that has great industrial and academical interest for its amazing properties combination that includes transparency, thermal stability and optical properties. It is also one of the engineering polymers with the highest impact resistance and is known as the

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F. L. B. Omena de Oliveira (✉) · M. C. A. Moreira Leite · L. O. Couto · T. R. Correia
Instituto de Química, Universidade do Estado do Rio de Janeiro, Rua São Francisco Xavier 524,
Maracanã, RJ 20550-900, Brazil
e-mail: flaviaomena@gmail.com

transparent material with the highest toughness [1]. These characteristics give to PC a large range of applications.

The properties of a particular material will determine its applications and an important polymer characteristic which affects its properties is the amorphous or crystalline (semicrystalline) state. Amorphous polymers tend to exhibit, for example, a lower chemical resistance, while semicrystalline ones tend to handle solvents action better. Polymer chains organization differences create particular properties that could interfere on the general applications of those materials.

Crystallizable polymers are divided according to its difficulty upon crystallization. For instance, polyethylene is characterized by its easy and spontaneous crystallization, even under a quenching procedure. Polymers as polypropylene can be amorphous or crystalline according to its manufacturing and processing conditions. PC belongs to a group of polymers which, even though crystallization can be achieved, this is a slow and difficult process [2]. For the last two classes of polymers mentioned before, the chain mobility increase can lead to polymer crystallinity induction.

Along the years, various methods have been used to obtain crystallinity induction on PC samples. Thermal induction is considered extremely slow and it was studied by Turska et al. [3] who obtained a crystalline degree of about 18–28% for PC samples thermally treated at 190 °C for 170 h. Plasticizers were also used on crystallization studies as described on Liang et al. work [4], where diallyl orthoftalate (DAOP) promotes crystallinity induction in addition to a plasticizer effect. The exposure of such polymer to an acetone vapor-saturated environment has generated crystallinity induction after a 2-h treatment [5]. Although crystallinity induction is studied on controlled environment and conditions, it is important to remember that such phenomenon can occur undesirably at working conditions and this can cause a modification on the artifact characteristics, damaging its performance.

Multiple melting behavior is a characteristic presented by some flexible or semiflexible semicrystalline polymers, such as PET, PBT, PEEK, and PSi [6]. On PC samples, literature reveals the presence of two distinct endothermic peaks, under specific crystallization conditions [6–8]. This characteristic is often explained as consequence of reorganization process during heating or the existence of two or more crystal populations which have distinct thermal stability, but the occurrence of this phenomenon is not completely elucidated yet [7].

The purpose of this article was to analyze samples of different molar masses bisphenol-A PC crystallized by acetone vapor using techniques as differential scanning calorimetry (DSC), Fourier transform infrared spectroscopy (FTIR), polarized light microscopy (PLM) and scanning electron microscopy (SEM) and testing their mechanical properties.

Experimental

Materials and samples preparation

In this study were used Bayer PCs (Makrolon 2458, MFR = 20.0 g/10 min; Makrolon 3108, MFR = 6.5 g/10 min), dried for 24 h prior the use. Melting flow rate (MFR) represents a measure that quantifies the polymer flowing ability, therefore can be related to its molar mass. Given a determined period of time, as higher is the amount of polymer that flows, lower is its molar mass. PC samples were obtained through solvent casting and compression molding and further analyzed as following described.

Solutions with 1, 3, and 5% of PC on chloroform were prepared and cast on a glass surface. The films obtained by this method were then demolded after 24 h solvent evaporation.

Compression molded samples of the two molar mass samples were obtained following ASTM D638 (type V) [9], on a Carver press with water circulation. Samples were molded under 7 ton of pressure at 245 °C for 10 min and then cooled to room temperature at the same pressure.

Crystallinity induction

Cast films and compression molded samples were submitted to acetone vapor-saturated environment for 24 and 48 h, respectively. After the exposure, the samples were dried for 24 h (cast films) and 96 h (compression molded) at room temperature before the analyses were performed.

Measurements

All data were collected before and after acetone vapor exposure. Cast film samples morphology was observed by Olympus MIC-D microscope under polarized light. Those samples were sealed on aluminum pans and analyzed on a Perkin Elmer Pyris 1 DSC. Temperature scan were performed from 80 to 280 °C, under nitrogen atmosphere on a 20 ml/min flow, at a rate of 20 °C/min. FTIR analysis was made on a Perkin-Elmer Spectrum One device, using Attenuated Total Reflectance (ATR) technique, without any previous treatment. The film samples thickness was evaluated before spectroscopic analyses, since it can interfere on ATR results. All films were measured with a micrometer and presented approximated thickness of 0.01 mm.

Compression molded samples were also analyzed on the same DSC equipment, but at a rate of 10 °C/min, with all other conditions unchanged. The surface of compression molded samples was coated with gold in order to have their morphology observed on a Carl Zeiss LEO 1450 VP Scanning Electron Microscope, under 10 kV electron acceleration voltage. Those samples were also submitted to a strain–stress test according to ASTM D638 (type V) on an EMIC model DL3000 equipped with a 1-kN load cell, at a crosshead speed of 10 mm/min. Fracture surface of the tested samples was observed by an Olympus MIC-D microscope under reflected light.

Results and discussion

Samples codes and obtaining conditions are listed on Table 1. After the acetone vapor exposure, all cast film and compressed molded samples exhibited alteration

Table 1 Polycarbonate samples preparation and codes

Sample form	PC grades and amount		Vapor exposure period (h)	Sample code
Cast films	Makrolon 3108	1%	–	FA1
	(MFR = 6.5 g/10 min)		24	FA1-24
		3%	–	FA3
			24	FA3-24
		5%	–	FA5
			24	FA5-24
	Makrolon 2458	1%	–	FB1
	(MFR = 20.0 g/10 min)		24	FB1-24
		3%	–	FB3
			24	FB3-24
		5%	–	FB5
			24	FB5-24
Compression molded	Makrolon 3108		–	CA
			48	CA-48
	Makrolon 2458		–	CB
			48	CB-48

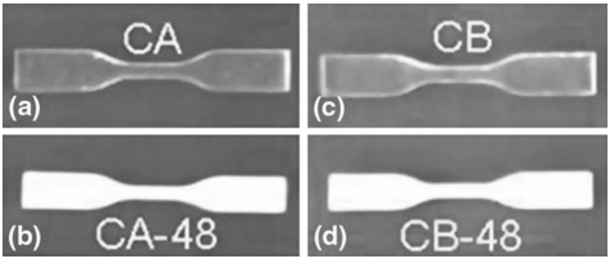

Fig. 1 Photography of compression molded samples: before (**a** higher molar mass PC and **c** lower molar mass PC) and after 48 h of acetone vapor exposure (**b** higher molar mass PC and **d** lower molar mass PC)

on their visual aspect, changing from transparent to opaque patterns at the end of the treatment, as observed on Fig. 1. This behavior can indicate that there is a crystalline phase coexisting with the amorphous phase, since semicrystalline polymer tend to be opaque due to light refraction index differences between crystalline and amorphous phases [10].

Measurements

PLM analysis

Figures 2 and 3 show cast film samples observed under polarized light. As can be seen, the micrographs obtained before the acetone vapor exposure did not present

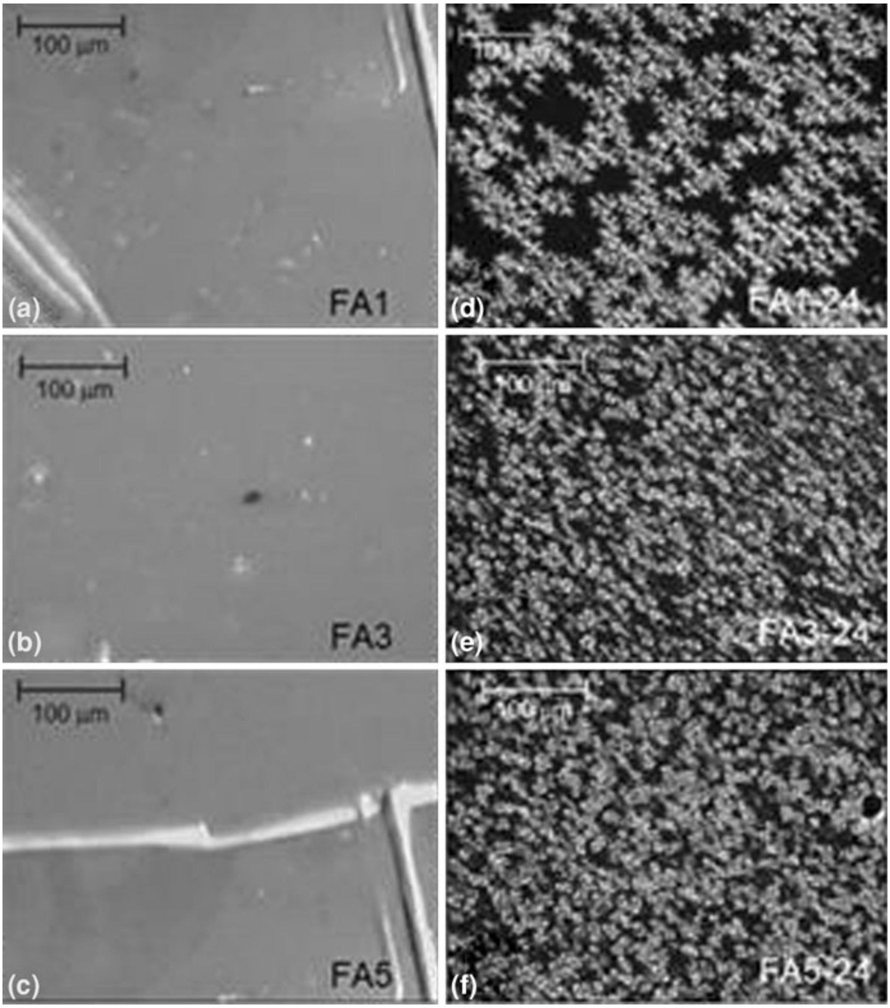

Fig. 2 PLM micrographs from higher molar mass film samples: before (**a** 1%, **b** 3%, and **c** 5% of PC) and after 24 h acetone vapor exposure (**d** 1%, **e** 3%, and **f** 5% of PC) (magnification: ×40)

crystalline structures, exhibiting a smooth texture. In this case, it was only possible to distinguish some imperfections of the glass slide. After a 24-h exposure period, however, the samples presented dark and light patterns, which occur when there is a phase contrast. This observation proves the coexistence of crystalline and amorphous phases on these samples. Maltese-cross structures (spherulites) commonly referred as to semicrystalline polymer phase structures were effectively visualized on the higher molar mass sample films (Fig. 2). This suggests that spherulite size is affected by the polymer molar mass and it tends to be bigger at films with higher molar mass when compared to the ones of lower molar mass.

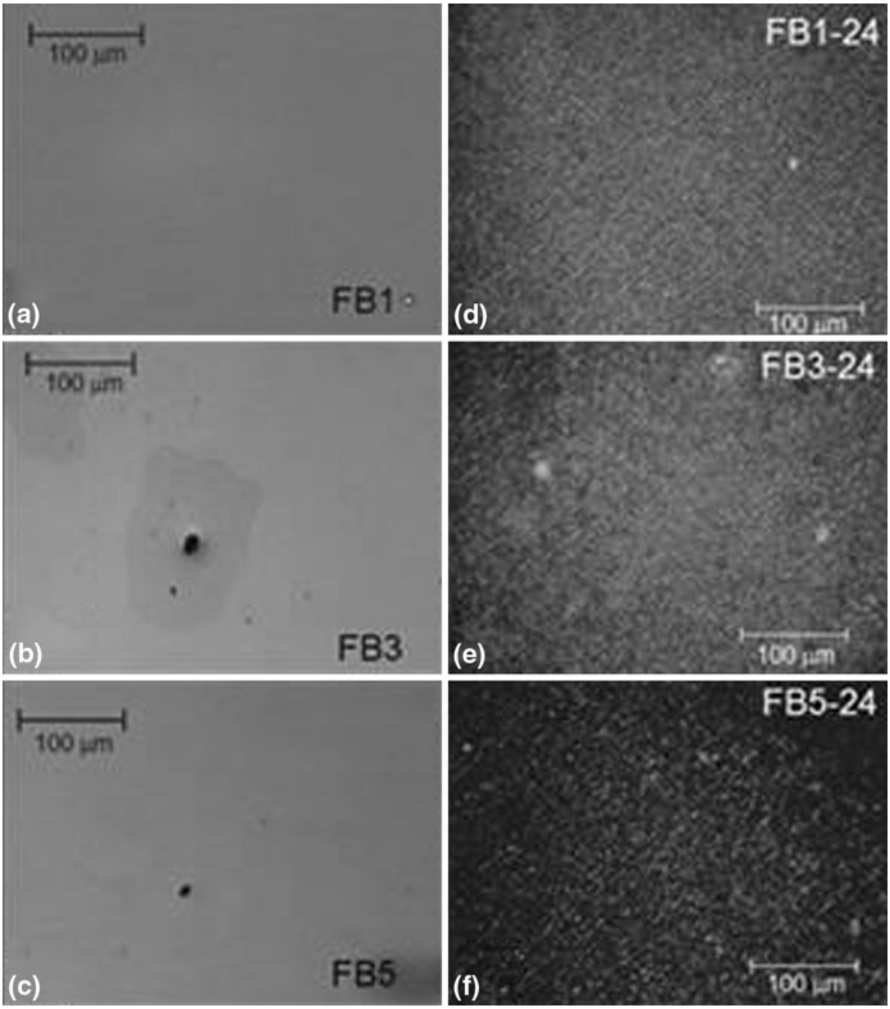

Fig. 3 PLM micrographs from lower molar mass film samples: before (**a** 1%, **b** 3%, and **c** 5% of PC) and after 24 h acetone vapor exposure (**d** 1%, **e** 3%, and **f** 5% of PC) (magnification: ×40)

DSC measurements

All samples prior to exposure did not present melting peaks and it was only possible to observe the glass transition temperature (T_g) through DSC analyses as shown on Fig. 4. Samples exhibited T_g near to 150 °C, as seen in previous articles [1].

After 24-h exposure, cast film samples showed transition related to the crystalline phase. Figures 5 and 6 show DSC curves for the two films series, all treated for 24 h by acetone vapor. It can be seen that those curves present a multiple melting behavior, as described on previous works with acetone use [11, 12]. The general aspect of these curves did not show a significative pattern change for the different

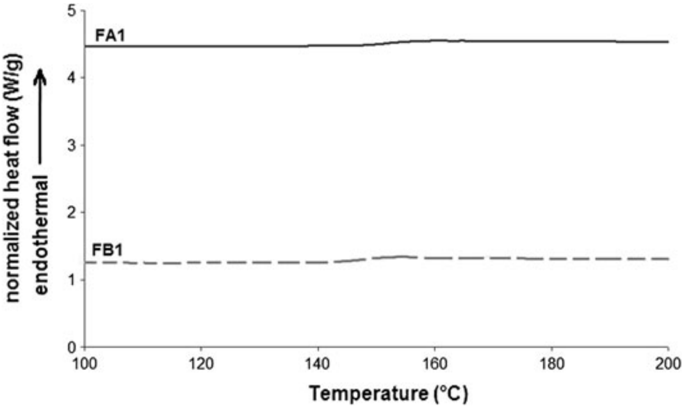

Fig. 4 DSC curves for the glass transition temperatures of film samples for higher (*solid line*) and lower (*dashed line*) molar mass PC before acetone vapor exposure

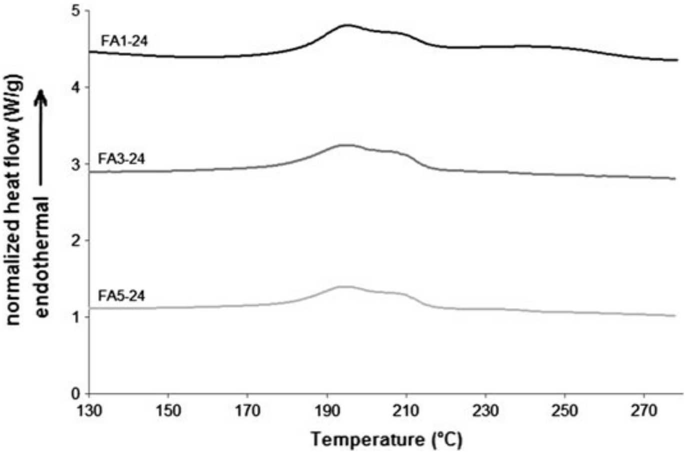

Fig. 5 DSC curves for the melting temperatures after acetone vapor exposure for 24 h for higher molar mass films with 1% (*top*), 3% (*middle*), and 5% (*bottom*) of PC

molar mass PC samples studied on this work, indicating similar melting behavior for all films.

According to Table 2, it can be observed that only for the film with 1% of PC there is a significant difference between the melting enthalpy values. Enthalpy related to the melting transition of each film, considering both peak transitions together, had a considerable increase with the increase of the molar mass. This result corroborates with the micrographs previously mentioned, where it could be observed that crystalline structures of bigger size and better definition were seen on the higher molar mass film, which justify a higher amount of energy to melt them and a higher crystallinity degree. No differences on T_m values were found among the films transitions.

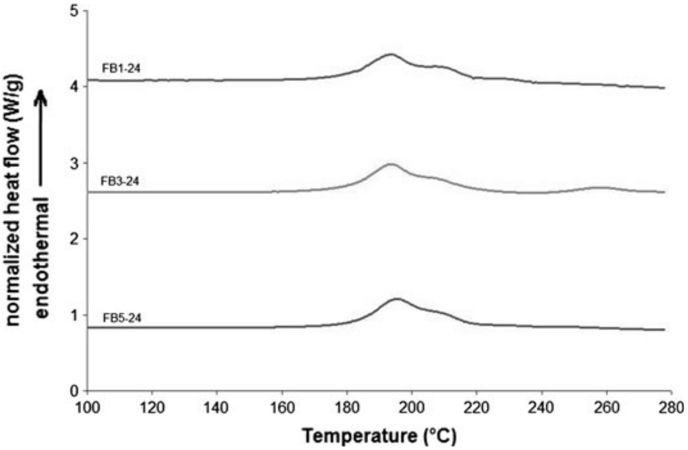

Fig. 6 DSC curves for the melting temperatures after acetone vapor exposure for 24 h for lower molar mass films with 1% (*top*), 3% (*middle*), and 5% (*bottom*) of PC

Table 2 DSC results from PC film and compression molded samples

Sample	T_{m1} (°C)	T_{m2} (°C)	ΔH_m (J/g)
FA1-24	195	208	55
FB1-24	194	207	28
FA3-24	195	204	29
FB3-24	194	206	30
FA5-24	195	206	30
FB5-24	195	207	29
CA-48	210	–	54
CB-48	208	–	35

DSC analysis of the compression molded samples after exposure to acetone vapor (Fig. 7) also presented peaks related to the crystalline phase melting which were not found at the non-exposed ones. There is still a tendency to obtain a higher enthalpy of melting for the sample with a higher molar mass, as verified for the cast films. It could also be observed on Fig. 7 a deviation from the baseline close to glass transition temperature and prior to the melting temperature (T_m), probably caused by some trapped solvent that leaves the polymer due to chain mobility.

FTIR measurements

Before exposure, all the films showed basically the same absorptions of a typical PC spectrum [13]. Figure 8 shows spectra of PC for the higher molar mass films samples before and after acetone vapor exposure. There could be identified bands on 2874 and 2969 cm^{-1} related to methyl groups C–H bond stretching vibrations and on 1364 and 1386 cm^{-1} related to its bending vibrations. Other bands are observed on 1465 cm^{-1} (related to C–H bending vibrations of methylene groups) and on

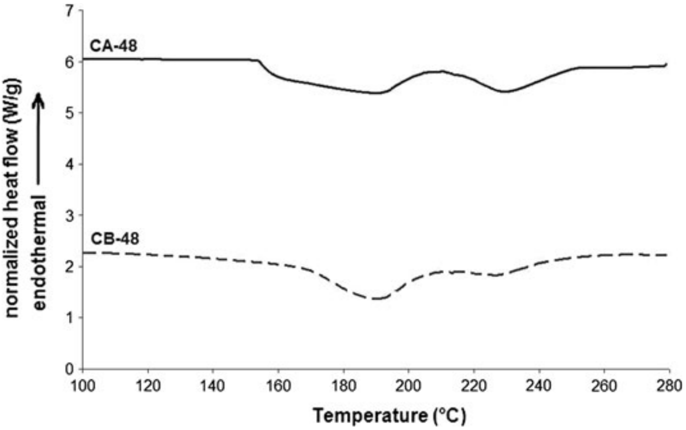

Fig. 7 DSC curves from compression molded samples after acetone vapor exposure for 48 h for higher (*solid line*) and lower (*dashed line*) molar mass PC

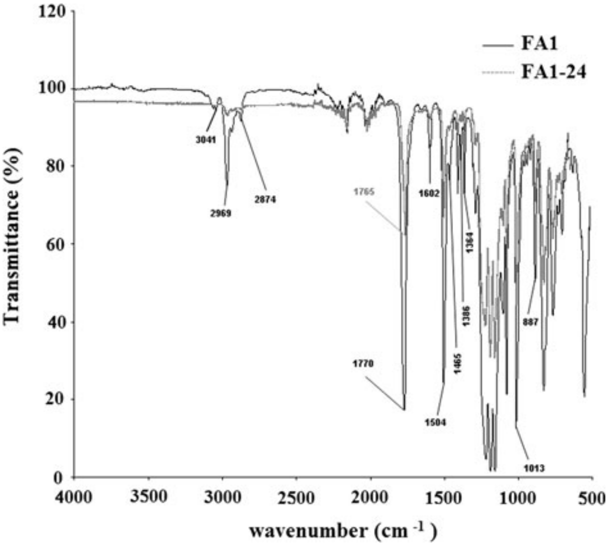

Fig. 8 FTIR spectra for higher molar mass films before (FA1) and after (FA1-24) acetone vapor exposure for 24 h

1770 cm^{-1} (corresponding to C=O stretching vibrations absorption band of ethers). Aromatic p-substituted ring absorptions appear on 3041, 1602, 1504, and 1013 cm^{-1}, and asymmetrical vibration of C–O–C bond appears on 887 cm^{-1}.

After 24-h exposure, ATR spectra have shown similarities among all film samples. As seen in previous work for crystallized PC [14], carbonyl band has shifted from 1770 to 1765 cm^{-1} and bands intensities also have shown a significant decrease. Due to crystallinity induction polymer chains are more closely packed which may cause restriction to functional group vibration and consequently a decrease on band intensity occurs. Similar behavior was seen for poly(L-lactic acid) C–O–C bands [15].

SEM analysis

Figure 9 shows SEM micrographs obtained for the lowest molar mass compression molded sample, before and after acetone vapor exposure for 48 h, that describes the overall behavior of the tested samples.

SEM analyses showed differences on the surface of the samples before and after the treatment. It could be observed a slight rugosity after the exposure in contrast with the smooth texture exhibited before the treatment. However, the crystalline phase structures could not be seen through SEM.

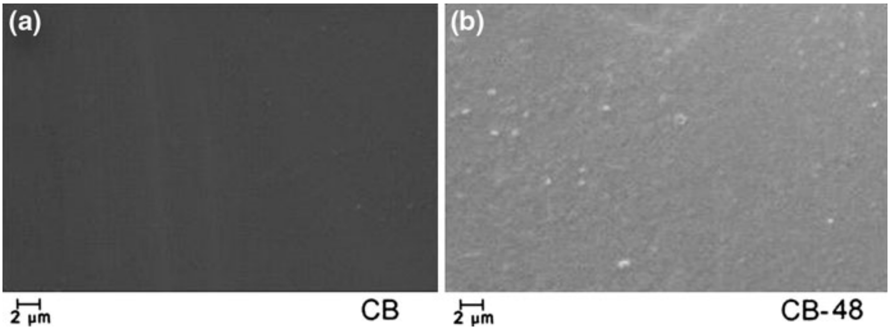

Fig. 9 SEM compression molded samples: **a** before (CB) and **b** after (CB-48) acetone vapor exposure for 48 h (magnification: ×3,000)

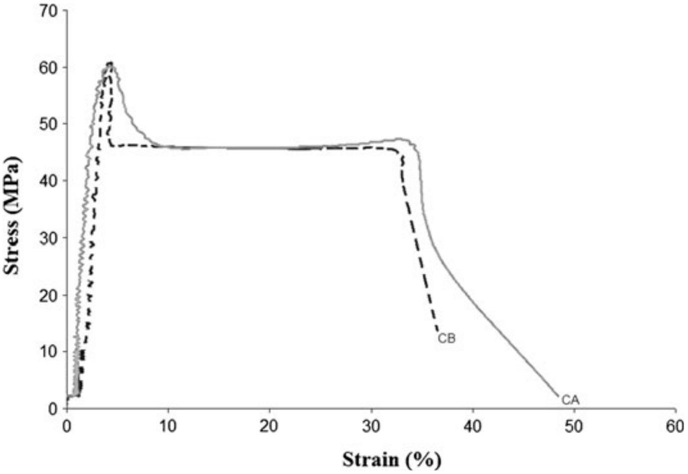

Fig. 10 Mechanical behavior from higher (CA) and lower (CB) molar mass compression molded samples before acetone vapor exposure

Mechanical properties measurements

Polycarbonate is expected to behave as a ductile polymer, according to literature data [16]. The profile observed for the compression molded samples submitted to mechanical tests prior to the crystallinity induction was the same reported in such papers. After the treatment, both PC molar mass samples studied have presented a profile similar to fragile materials, where no flexibility was observed. Figures 10 and 11 show the stress–strain tests for both samples, before (Fig. 10) and after acetone vapor exposure (Fig. 11), where can be observed the decrease on mechanical performance for those that had their crystallinity inducted. However, there was no significant difference on mechanical performance between the different molar mass samples of PC studied. Reflected light micrographs taken from the fracture of those samples have confirmed the behavior changing from ductile to fragile fractures after vapor acetone exposure, as seen on Fig. 12.

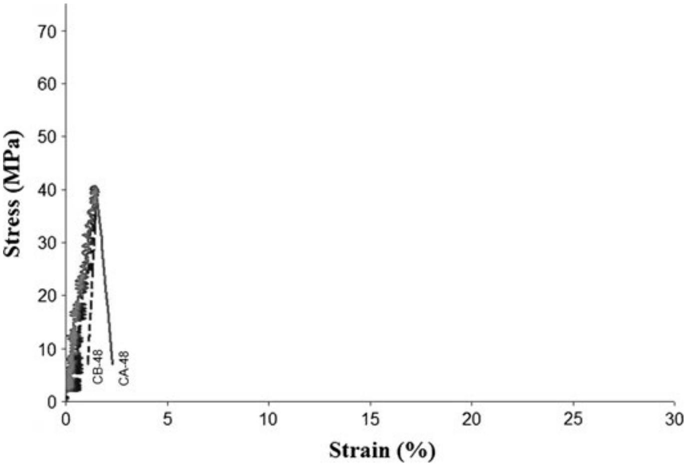

Fig. 11 Mechanical behavior from higher (CA-48) and lower (CB-48) molar mass compression molded samples after acetone vapor exposure for 48 h

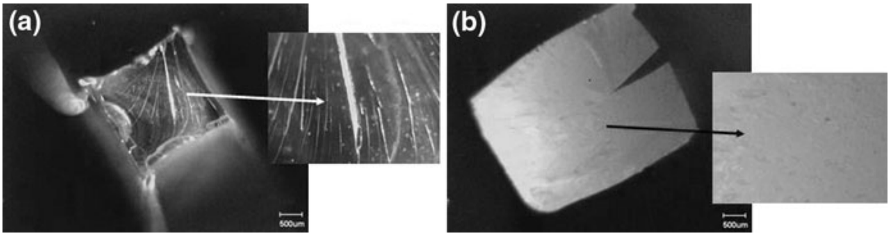

Fig. 12 Optical microscopy of compression molded lower molar mass PC sample fractures: **a** before and **b** after acetone vapor exposure for 48 h submitted to mechanical tests (magnifications: ×22 and ×75)

Conclusions

Crystalline phase structure morphology of the studied PCs samples is spherulitic and its size is driven by the polymer molar mass. For the highest molar mass, PC samples were obtained the highest energy amount of enthalpy of melting, indicating the highest crystallinity degree, with values extremely close for compression molded and 1% PC cast film. The highest molar mass sample originates spherulites with bigger size and better definition than the sample of lowest molar mass. This behavior probably happens because of the high-constitutional repeating units number on PC structure, leading to a great number of folding sites for those samples.

Overall, the crystallinity induced on PC film samples has promoted a restriction to the functional groups vibration that could be seen as an intensity decrease on FTIR spectra, also accompanied by a shifting on carbonyl frequency to a lower value.

The mechanical resistance of compression molded samples decreases after the crystallinity induction on both PC grades studied on this article. The crystalline profile acquired by PC samples leads to modifications on the polymer morphology that interferes on PC properties. These modifications could induce the occurrence of flaws during application, depending on the environment to which the material is submitted.

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