TMA and DSC study of molded and annealed polyester : a thermal expansion and crystallization evaluation

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خلاصة

استخدمت تقنيات التحليل الميكانيكي الحراري TMA و المسح التفاضلي DSC لدراسة تأثير قولبة وتلدين البولي استر على سلوك التمدد الحراري والتبلور حيث إن هذه العوامل تلعب دورا في عمليات الإعادة او الاسترجاع للبوليمر. يزود التحليل الميكانيكي الحراري بالطريقة الديناميكية معلومات تشخيص متقدمة حول البوليمر حيث تقوم بفصل الانتقالات إلى إشارات قابلة للعكس وغير قابلة للعكس إضافة إلى إظهار التقدم الحاصل في المناطق العشوائية عندما يفقد البولي استر المقاومة الميكانيكية مع درجة الحرارة بالاقتراب إلى نقطة الانصهار. يحدث التبريد البطيء للبوليمر بعد التلدين تبلور يمكن أن يعزى إلى استقامة السلسلة الجزيئية من جراء التوجيه.

ABSTRACT

Thermomechanical analysis (TMA) and differential scanning calorimetry (DSC) are used to investigate the effect of molding and annealing of polyester on the behavior of thermal expansion and crystallization since these factors play role in the reprocessing or recycling of the polymer. The dynamic mode of the TMA provides enhanced characterization information about the polyester since it separates the transitions into reversible and irreversible signals, and also reveals the progress of the amorphous regions as the polyester loses strength with the increasing temperature approaching melting. Slow cooling after annealing brings crystallization that may be attributed to molecular chain straightening due to orientation.
Keywords: TMA, DSC, Recycling, Crystallization, Thermal Expansion

INTRODUCTION

Polyesters are well known polymers that have many major industrial applications. Current work is being devoted on presenting efficient solutions for the problems encountered in recycling or reuse of these materials since they are not biodegradable. As chemical processing is most often costly and some times aggressive to the environment, a possible solution is the recycling of such material by thermomechanical techniques. [1] Chemically modified polyethylene terephthalate with a new diepoxide chain extender has been studied by dynamic thermomechanical and tensile properties [2]. The application of modulated – temperature progressing to thermomechanical analysis has been investigated by Price [3]. The analysis affords method for separating the reversible nature of thermal expansion from irreversible deformation arising from creep under the applied load or change in dimension due to relaxation of orientation.
Polyester samples subjected to special schemes of crystallization annealing treatment at multiple descending temperatures by DSC show

multiple melting points which were demonstrated to be the effect of multiple lamellae population [4]. On the other hand cold – drawn polyester annealed at different undercoolings investigated by DSC and DMTA show that the onset of Tg region in the cold – drawn, un – annealed is found to be lower than in the case of un – oriented PET [5].   An investigation to explain the evolution of annealing process of injection molded semi-crystalline polyester by the correlation of structural characteristic from FTIR and DSC results   [6] have shown to be influenced by the lamellae structure. In an attempt to further explain the unfolding of lamellae structure during molding and annealing cycles, thermomechanical analysis TMA is employed [7].

The aim of the present study is to evaluate some of the thermal parameters of the treated polymer that can eventually be fed in the reprocessing of the polymer to obtain for instance blend or composite materials for engineering applications.

Experimental

Raw granules of the polymer (obtained from local market) were molded in a vacuum oven at 280 °C into a bulk shape which was then machined into bars of diameter 8 mm and length 20 mm. The bars were annealed in vacuum oven in the temperature range 200 – 220 °C for 20 minutes and then slowly cooled in the oven to room temperature. Thermomechanical analysis were made on Linsies type PT 1000 in static penetration mode and dynamic penetration mode at constant initial loading of 1N and sinusoidal wave of 0.5N in amplitude and 0.5Hz in frequency. The differential scanning calorimetry were made on Shimadzu DSC – 60 analyzer at a heating rate of 10°/min with some samples flushed with nitrogen gas and others without nitrogen flushing.

Results and Discussion

TMA – static mode

Figure 1 shows change in sample length (ΔL) and   thermal expansion coefficient (def. $\alpha = \Delta L / L \Delta T$)curves as a function of temperature. The ΔL curve show non-linear behavior in the temperature range 30-200 ^{o}C, where ΔL increases rapidly beyond the glass transition temperature (70°C). The behavior can be explained as lamellae forming the molecular chains starts to unfold as glass transition is crossed leaving the unfolding to progress steadily to unoriented like molecular chains.
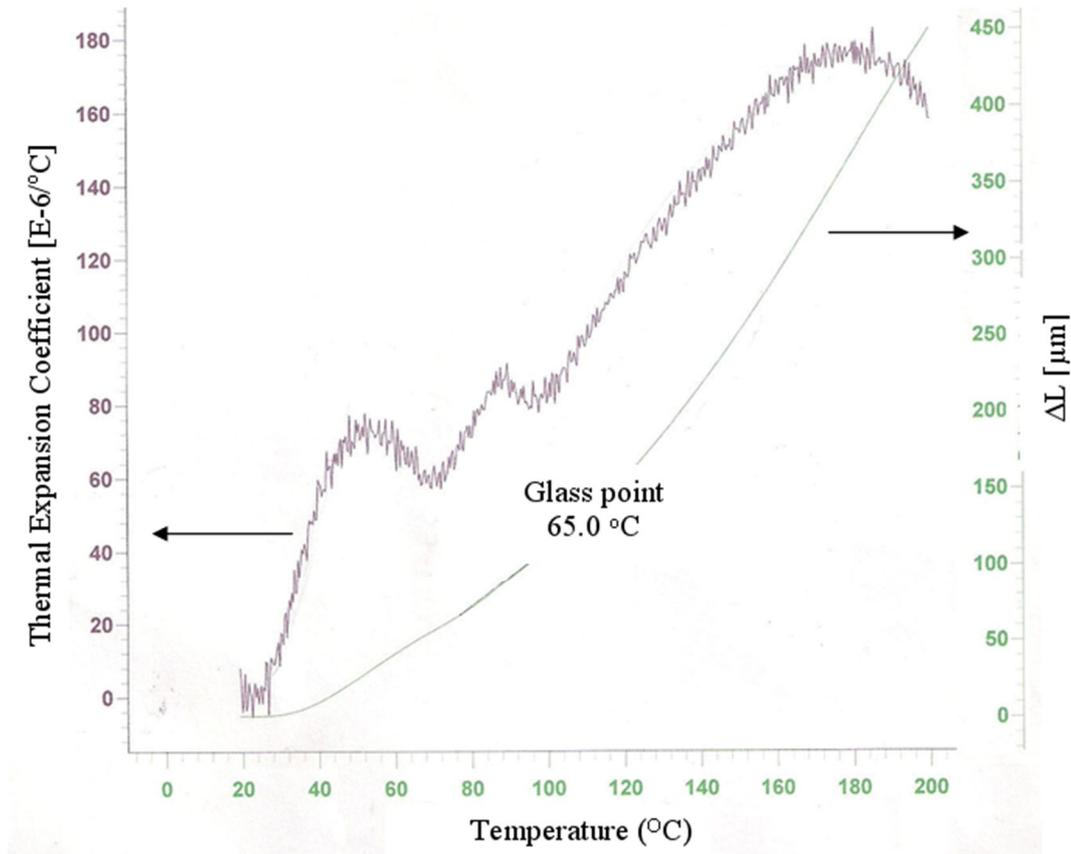
Figure -1 : Change in length and thermal expansion of polyester in static mode (TMA test)

The thermal expansion curve also features three distinct regions. From room temperature (30°C) α rises sharply in a behavior similar to crystalline materials. The behavior change at the glass transition to viscous as softening begins to take effect and at higher temperatures, the curve flattens out for large α`s. The inflection of the α curve near 175°C is a consequence of irreversible deformation arising from creep due to relaxation of orientation [3].

The thermal expansion coefficient (α) in the 1st region up to 50 °C is 70×10^{-6} °C^{-1}, in the 2nd region up to 90 °C is 85×10^{-6} °C^{-1}, and in the 3rd region up to 175 °C is 170×10^{-6} °C^{-1}. These values are inline with the values found in the literature [8] where αT for this polymer is about 1×10^{-6}. The decrease in α values at the glass transition temperature (70 °C) is a consequence of the transformation of material from crystal-like behavior of expansion to non-crystal like (amorphous) behavior of expansion which is clearly seen in the molecular chain structures of polymers.

TMA – dynamic mode

Figure 2 shows changes in sample length (ΔL) and thermal expansion curves as a function of temperature. The overall behavior of the ΔL curve in the dynamic mode is similar to that in the static mode regarding the progress in the changes in length with temperature, however the net change in length in the dynamic mode is larger than in the static mode by about 7% due to excessive loading. The curve also shows sinusoidal wave that progresses in the rate of penetration with temperature due to the viscous behavior of the molecular chains.
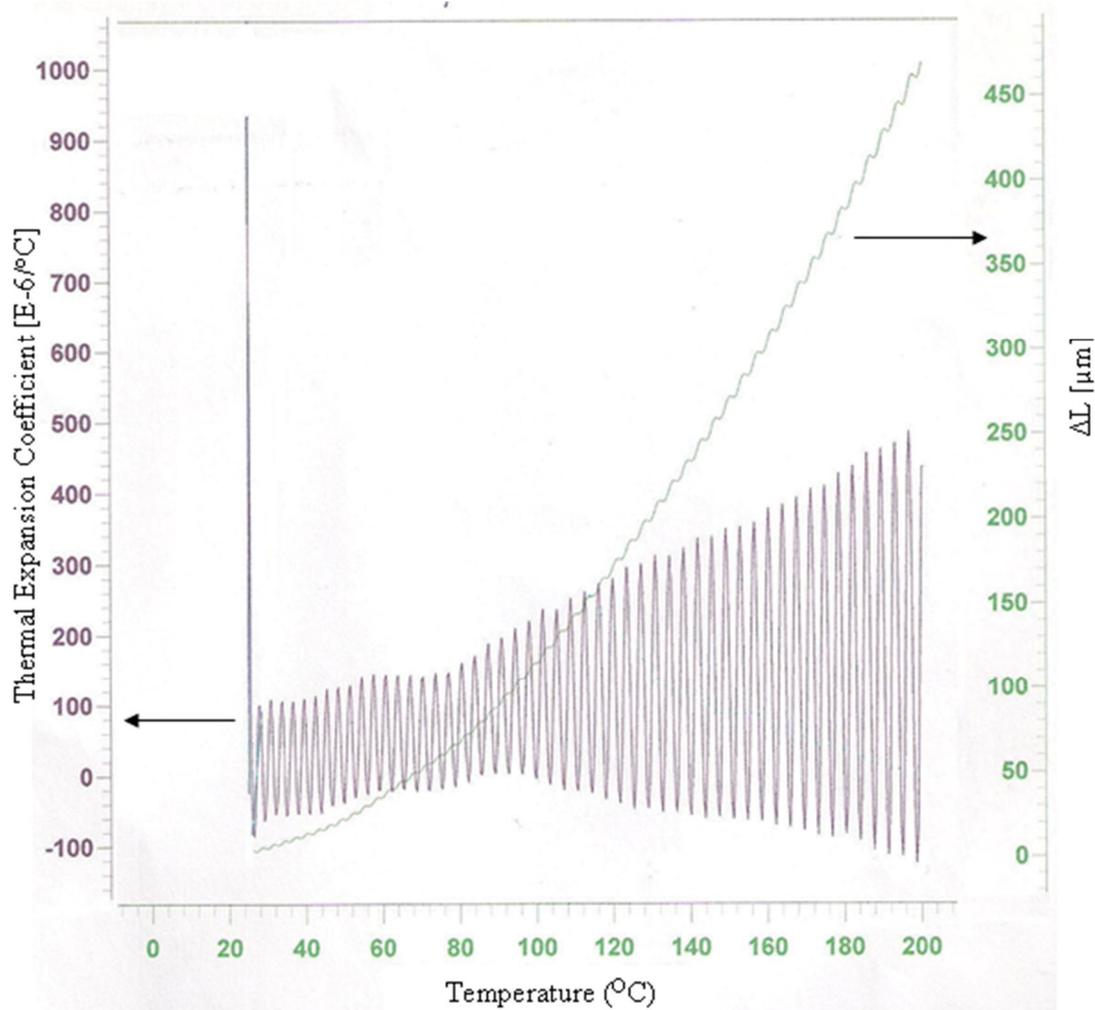
Figure -2: Change in length and thermal expansion of polyester in dynamic loading (TMA test) penetration mode, 1N constant load plus sinusoidal wave amplitude 0.5 N at 0.5 Hz.

The sinusoidal pattern of thermal expansion show typical viscous behavior manifested by regular increase in wave amplitude a above glass transition with temperature up to 200°C. A small crest at ~70°C identify the glass transition of the polymer.

Prior to Tg, however, the wave amplitude is constant an indication to a behavior of solid crystalline material. Thermal expansion coefficient values (α) in the dynamic mode at different temperatures are similar to those in the static mode.

Figure 3 shows DSC curves represented by heat flow (def. as the energy supplied to sample in Joules during the heating rate cycle) versus temperature for samples as molded and as annealed after molding. The general features in the as molded polyester signify glass transition point at 68°C and melting at 252°C. However in the annealed after molding, the DSC curve signifies the appearance of recrystallization peak at 125°C. This is due to the effect of annealing that brings orientation in the molecular chains.
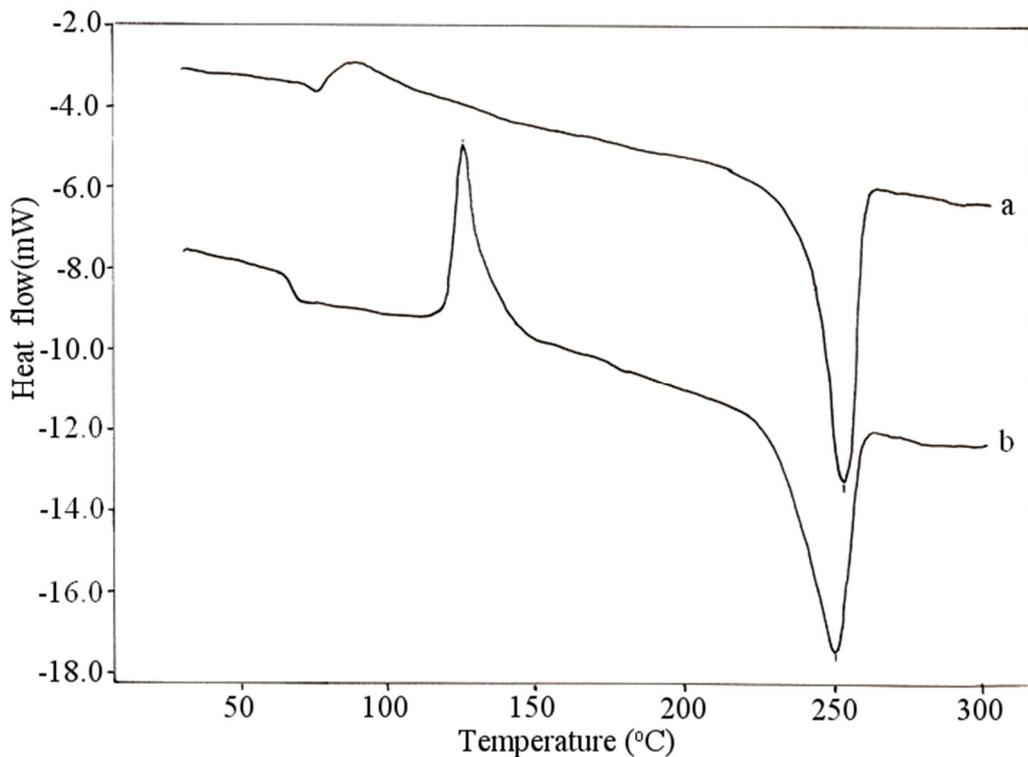
Figure 3: DSC Curves for polyester in normal air atmosphere (a) molded, (b) molded and annealed

This means that annealing has improved orientation and thus enhances crystallization.

Heat of melting ΔHm (calculated from the area under the peak in the DSC curve) of the molded sample (Figure 3a) is 61.16 J/g, compared with 36 J/g for the annealed sample (Figure 3b). Heat of crystallization ΔHc of recrystallized polyester is found to be 17 J/g. The decrease in the heat of melting for the annealed polyester is a consequence of crystallization in the molecular chains that were otherwise being amorphous in the molded samples and thus need more heat energy for melting. This means that heat of melting involve mostly amorphous regions which are more abundant in the molded polyester samples.

The DSC scans are also found to be slightly influenced by the presence of gas during the pursuit of measurement. It can be seen from Table 1 that Tg, Tc and Tm in the N_2 gas are less on average by 1.5 ± 0.7 °C from those with out gas.

Table 1: Values of glass transition, crystallization and melting temperatures and enthalpy of crystallization and melting for molded and annealed polyester in N_2 gas and without gas.

		Molded		Annealed	
		With N_2 gas	Without gas	With N_2 gas	Without gas
Tg (°C)		67.02	68.21	67.22	68.40
Tc (°C)	onset			120.14	120.79
	peak			124.55	125.79
Tm (°C)	onset	242.15	242.42	234.44	234.50
	peak	251.07	252.42	249.51	250.91
ΔHc (J/g)				14.44	16.98
ΔHm(J/g)		58.32	61.16	33.79	36.96

The heats of crystallization and melting appear to be more sensitive to the presence of N_2 gas, since it inhibits oxidation reactions that can occur during the heating cycle. Thus ΔHc and ΔHm are lower in the N_2 gas case (see Table 1).

CONCLUSION

TMA analysis convey the viscous nature of the polymer understudy when subjected to simultaneous dynamic loading and thermal effects. Evaluation of thermal parameters (ΔL and α) can be utilized in the subsequent processing or recycling of the polymer.

In the static TMA analysis, the method affords a mean for separating irreversible deformation (ΔL) from reversible nature of thermal expansion.

The DSC scans reveal the crystallization nature of the polymer chains when subjected to heat treatment.

The TMA analysis surpasses the DSC scan in revealing the viscous behavior of the polymer and thus more appropriate for detailed evaluation.

Acknowledgment

REFERENCE

1. Avila, A.F., Duarte, M.V. "A mechanical analysis on recycled PET/HDPE composites", Polym. Degrad. Stabil., **80**(2): 373-382(2003).

2. Bikiaris, D.N., Karayannidis, G.P. "Dynamic thermomechanical and tensile properties of chain-extended poly(ethylene terephthalate)", J. Appl. Polym. Sci., **70**(4): 797-803(1998).

3. Price, D.M. "Modulated–temperature thermomechanical analysis", Thermochimica Acta, **357**: 23-29(2000).

4. Woo, E.M., Ko, T.Y. "A differential scanning calorimetry study on polyethylene terephthalate isothermally crystallized at stepwise temperatures : multiple melting behavior re-investigated", Colloid and Polymer Sciences, **27**(4): 309-315(1996).

5. Bartolotta, A., D, Marco, G., Farsaci. F., Lanza, M., Pieruccini, M., "DSC and DMTA study of annealed cold-drawn PET : a three phase model interpretation", polymer, **44**(19): 5771-5777(2003).

6. Quintanilla, L., Rodrignez-Cabello, J.C., Jawhari, T., Pastor, J.M. "Structural analysis of injection –modulded semi-crystalline polymer by FTIR with photoacoustic detection and DSC 1.PET", Polymer, **34** (18): 3787-3795(1993).

7. Karagiannids, P.G., Stergiou A.S., Karayannids, G.P. "Study of crystallinity and thermomechanical analysis of annealed

poly(ethylene terephthalate) films", European Polymer Journal, **44**(5): 1475-1486(2008).

8. ASM Handbooks, Vols.1 and 2. ASM International, Materials Park, OH. Properties of selected engineering materials , Appendix B, p. 805.