Effect of Heat Treatment on Changes In The Crystalline Domains In Mylar Film

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Abstract

Changes in the crystalline domains caused by heat treating Mylar films between Tg to 240 ^{o}C have been studied by Fourier Transform Infrared spectroscopy (FTIR) and X-ray Diffraction (XRD). Prior to glass transition temperature, shrinkage in the film is insignificant, but progresses rather abruptly as melting point is approached bringing the smooth film surface to rather wrinkle. The absorbance increase in the FTIR spectra is due to the thickened film caused by shrinking rather than the improvement in the crystalline orientation. XRD on the other hand show that heat treatment of the film near melting point only reduces the contribution of the crystalline domains in the direction [100] in favor of other direction namely $\left[1\bar{1}0\right]$ rather than on the account of loosing order in favor of the amorphous regions.

Keywords: Mylar film ; Crystalline domains ; FTIR ; XRD ; Crystallinity

تأثير المعاملة الحرارية على التغير في الحقول البلورية لفلم المايلر

الخلاصة

درست التغيرات في الحقول البلورية المتسببة من المعاملة الحرارية لأفلام المايلر بتحويل فورير للأشعة تحت الحمراء FTIR و حيود الأشعة السينية XRD. قبل درجة الانتقال الزجاجي ، يكون الانكماش في الفلم غير ملحوظ ، لكن يتقدم نوعا ما بشكل مفاجئ عند الاقتراب من نقطة الانصهار ليجلب سطح الفلم الصقيل إلى سطح متجعد. تكون الزيادة في الامتصاص في أطياف FTIR بسبب التثخن في الفلم جراء الانكماش بدلا من التحسن في التوجيه البلوري. من جهة أخرى تبيّن أطياف XRD بان المعاملة الحرارية للفلم قرب نقطة الانصهار تنقص فقط من مشاركة الحقول البلورية في التوجيه [100] لصالح توجيه أخر $\left[1\bar{1}0\right]$ عوضا عن فقدان التوجيه لصالح المناطق العشوائية.

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1. Introduction

Mylar and Melinex are the trade names of films manufactured from the polymer polyethylene terephthalate (PET). The film exhibit high tensile strength, dimensional stability, optically transparent and good electrical insulation. The leading application of these films are their use in packaging and in many other uses [1].

Crystalline domains (regions) in Mylar film prepared by calendaring process contain high percentage of crystalline orientation and low percentage of amorphous regions. Small angle X-ray scattering (SAXS) and wide angle X- ray scattering (WAXS) are routinely used in the evaluation of crystalline structures and degree of crystalline orientation (crystallinity) in polymers [2]. The method of WAXS has been modified for the determination of crystallinity in polymers [3]. In connection, the study of crystallinity and thermo-mechanical analysis of annealed poly(ethylene terephthalate) film is being reported [4].

Recently work is being devoted on the evaluation of crystallinity by Fourier Transform Infrared (FTIR) spectroscopy. Off these, a novel FTIR method for determining the crystallinity of poly (ε- caprolactone) [5], of syndiotatic polystyrene [6,7], of heat set and drawn polyamide 66 fibers [8]. ASTM has reported a test method for measurement of the percentage of crystallinity of polyetheretherketone (PEEK) polymers by means of specular reflectance FTIR [9]. As no work has been reported on the crystallinity of Mylar film by FTIR, the present work aims to shed some light on the utilization of FTIR spectra in the evaluation of degree of crystallinity in Mylar films in terms of changes occurred by the effect of heat treatment. WAXS or generally XRD is also employed as a complementary evaluation method.

Experimental

Ribbon Mylar film roll (Steiner Film®) of 60 mm width and about 6μm thick was used in this work. Fixed length film samples were heat treated between 70 to 240 ^{o}C for 20 minutes in a gradually heated oven to avoid sudden contraction. After treatment the final lengths were recorded. FTIR spectra for films treated at different temperatures were taken by using FTIR-Shimadzu 8400 spectrometer in the absorbance mode and wave number range 500-2500 cm^{-1} with resolution $2cm^{-1}$. Each spectrum was scanned repeatedly for 100 times to optimize signal to noise ratio. XRD scans were made on Shimadzu XRD 6000 diffractometer using monochromated Cu $K_{\alpha 1}$ radiation λ=0.15406 nm at a scan speed of 0.1 ^{o} s^{-1} and scan range $16<2\theta<34^{o}$ for the heat treated and non treated films.

Results and Discussion

Shrinkage

Films treated in the temperature range 70 to 240 ^{o}C show literally very little shrinkage around 70 ^{o}C, which is the glass transition temperature (Tg) of the polymer. Shrinkage however starts to increase rather sharply as the temperature is nearing the melting point of the polymer causing wrinkle appearance in the film surface. Such a large shrinkage is due to the contraction for both amorphous and consequently the crystalline region, because the Mylar film is highly biaxially oriented.

FTIR

FTIR spectra of treated Mylar films between Tg and 240 ^{o}C are

shown in Figure 1. The well resolved strong intensity peaks namely 728, 1022, 1340 and 1409 cm^{-1} are chosen for monitoring changes in absorbance that have been affected by heat treatment of the films. Changes in absorbance for the chosen peaks recorded in terms of treatment temperature are shown in Table 1. The results illustrate a consistent increase in the absorbance of the four peaks as the treatment temperature is raised irrespective of the location of the peak in the spectrum. It is suggested by Tadokoro et.al. [10], that changes in the intensity in the 1340 cm^{-1} peak is due to the configuration in the crystalline / amorphous regions. It is noted from Table 1 that the consistent build up in absorbance reflects that neither crystalline nor amorphous regions are affected by the treatment temperature and the increase in absorbance is merely a consequence of the thickened film arising from contraction due to temperature effect. This can be clearly seen in Table 2, which shows the average absorbance in the four peaks considered in Table 1 with the estimated standard deviations together with the shrinkage recorded in the films in terms of treatment temperature. The shrinkage in length reflects increased thickness on the film, thereby more absorption is noticed in the FTIR spectra. This can be interpreted as follows:

Since Mylar film is prepared with high degree of crystalline orientation, heat treatment which acts as an enhancing media for the amorphous regions to extend to more of crystalline regions seems to be of little effect in improving orientation in amorphous regions. But at the same time it has the deleterious effect of shrinking the film lengthwise and causing dimensional change in thickness. The results from these two independent parameters lead to comparable values. In the spectrum of Figure 1, the medium intensity absorption peak at 970 cm^{-1} is assigned by [10] to serve as a monitor to the development of the degree of crystalline regions present in the film. Moreover this peak corresponds to trans isomer of O-C-C group which is sensitive to crystallinity. By consulting Table 3 that presents changes in the absorbance intensities of the 970 cm^{-1} peak with temperature, it is clear that very little change in absorbance is noticed. This may look odd in comparison with the four absorption peaks considered earlier. This is because the four peaks are classified as strong intensity peaks whereas the 970 cm^{-1} peak is classified as medium intensity peak, thus changes in intensity of the latter are unnoticeable. Moreover, the change in the absorbance peak intensity is directly proportional to the amount of crystalline regions from which percentage in crystallinity can be calculated by taking the value of crystallinity in Mylar film at room temperature as 55% [4]. The results shown in column 2 of Table 3 reveal that crystallinity is slightly modified with the treatment temperature.

XRD

Figure 2 shows XRD profiles taken for the films at the specified temperatures corresponding to those in FTIR. It is clear that the profile of the (100) peak decreases in intensity with the increase of treatment temperature and at the 240°C another peak namely the $\left(\bar{1}10\right)$ begins to appear in counterpart to the (100) peak. This means that the crystalline

orientation manifested by the crystallographic direction [100] in the film at room temperature is affected by the temperature increase, causing some of the oriented crystalline domains of the (100) reflection to relax in particular orientation that forms the new profile peak $\left(\bar{1}10\right)$ .Moreover the appearance of $\left(\bar{1}10\right)$ reflection is accompanied by a decrease in the intensity of (100) reflection which is due to loss of preferred orientation when annealed at temperature near melting range. It should be emphasized that this transformation occurs in the crystalline domains only, and the associated changes in the amorphous regions are regarded as the change in the background hump of the profile in each case. Thus the semi-crystalline regions that are adjacent to crystalline and amorphous may play a role in the mechanism of transformation.

Conclusions

1. FTIR spectra serve to monitor the progress in crystalline / amorphous domains of Mylar films caused by heat treatment, but need to be used with caution and in conjunction with other methods like XRD or DSC.
2. XRD is the most appropriate method since it is directly involved in the detection of crystalline and amorphous structures as each structure is identified by long-range or short-range order.
3. The outcome of results indicate that heat treatment of Mylar films has little significance on the development of crystalline regions as the latter is being acquired by the nature of the chain structure of the polymer and the procedures of manufacturing the film.

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Table (1) Absorbance in various FTIR peak in terms of temperature for Mylar films.

T (^{o}C)	Absorbance (%)			
	728 cm $^{-1}$	1022 cm $^{-1}$	1340 cm $^{-1}$	1409 cm $^{-1}$
70	1.5	2.3	2.0	1.9
120	3.5	8.1	7.0	5.7
170	7.4	11.6	10.5	7.6
220	18.5	14.8	12.9	14.7
240	23.7	21.5	16.7	19.4

Table (2) Comparison between average absorbance from various peaks with shrinkage in Mylar films in terms of temperature.

T (^{o}C)	Average Absorbance(%)	Shrinkage(%)
70	1.9±0.5	0.8
120	6.1±3.4	2.4
170	9.2±4.1	8.1
220	15.2±4.5	16.3
240	20.3±4.5	24.2

Table (3) Changes in crystallinity of film from monitoring absorbance intensity in 970 cm $^{-1}$ trans configuration peak at different temperatures.

T (^{o}C)	IAbs (AU)	Crystallinity(%)
30	104.0	55.0
70	104.5	55.3
120	105.3	55.7
170	106.4	56.3
220	107.8	57.0
240	109.4	57.9

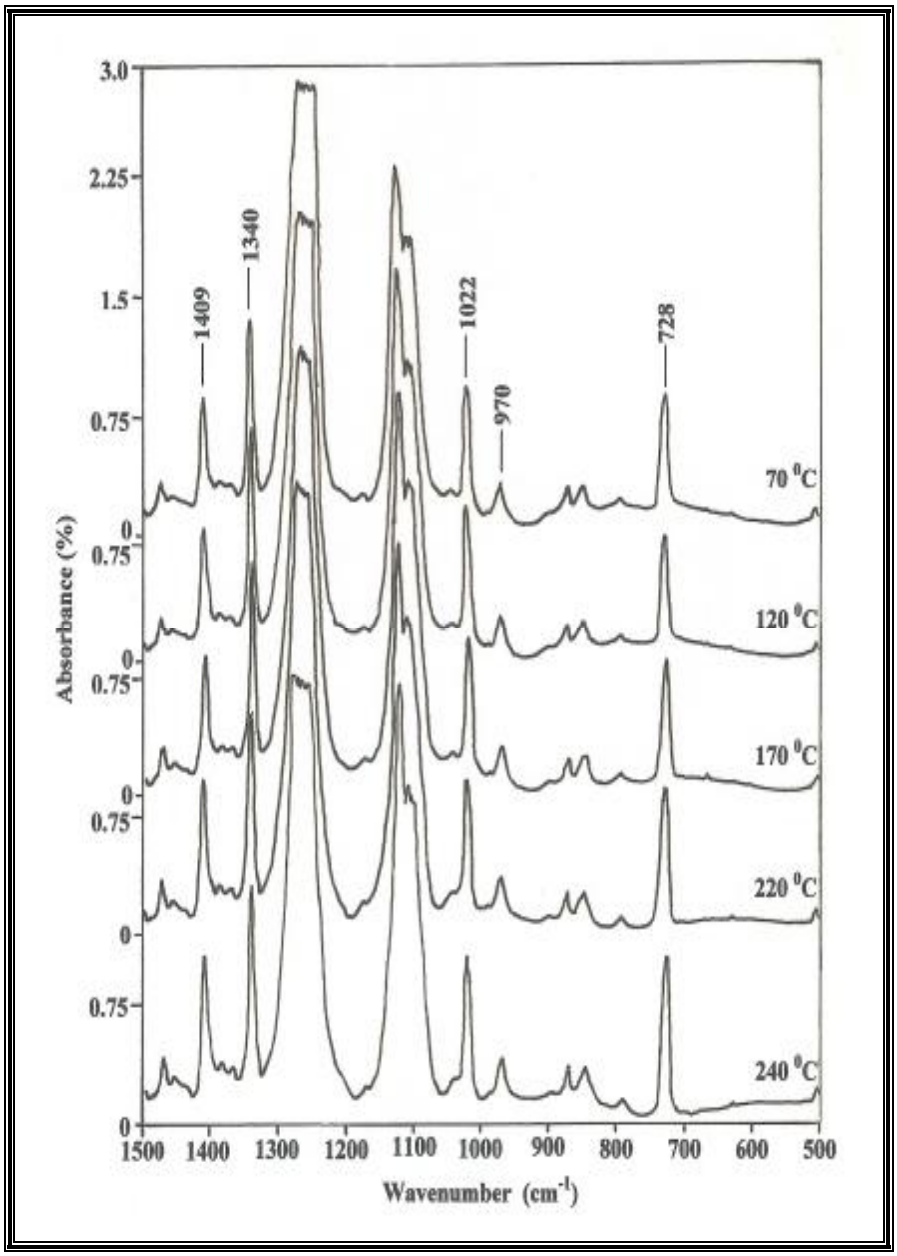

Figure (1) Absorbance FTIR spectra for heat treated Mylar films.

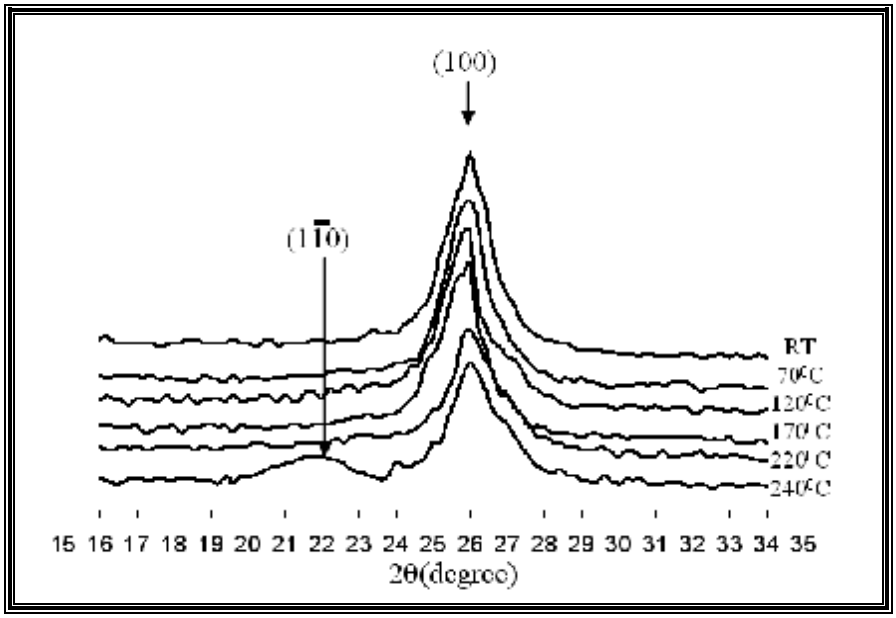

Figure (2) XRD profiles of Mylar films at different treatment temperatures.