

Bulletin of College of Engineering http://engineering.niu.edu.tw/main.php

國立宜蘭大學工程學刊第五期, 99-114 頁, 2009 年 3 月

Bulletin of College of Engineering, National Ilan University, NO. 5, P. 99-114, Mar.. 2009

# Effect of Annealing on an Amorphous Poly(ethylene terephthalate) Sheet

Hong-Bing Tsai<sup>1</sup> Da-Kong Lee<sup>2</sup> Ruey-Shi Tsai<sup>3</sup> Han-Yu Fang<sup>4</sup>

1. Professor, Department of Chemical and Materials Engineering, National Ilan University

2. Associate professor, Department of Chemical and Materials Engineering, National Ilan University

3. Associate professor, Department of Chemical Engineering, Da-Hua Institute of Technology

4. Master program, Department of Chemical and Materials Engineering, National Ilan University

#### Abstract

The effect of annealing on an amorphous poly(ethylene terephthalate) sheet is described in this article. Poly(ethylene terephthalate) (PET) sheet samples of different crystallinity were obtained by annealing originally amorphous PET sheets. The annealed PET sheet samples were characterized a differential scanning calorimeter (DSC), ultra-violet(UV)-visible spectrometry and X-ray diffraction. The PET sheet samples annealed at 80 or 100°C for 50 min remain amorphous. But the PET sheets annealed at 120°C or above for 50 min show significant crystallization. Thus, an annealing temperature of 110°C has been chosen for obtaining PET sheet samples of different crystallinity. It can be seen that as the annealing temperature or time increases, the crystallinity follows an increasing trend. The DSC and light transmittance data show that the crystallization rate after 40 min of annealing is much lower that before 40 min of annealing at 110°C.

Keywords: poly(ethylene terephthalate), crystallinity, annealing, thermal properties, light transmittance



Bulletin of College of Engineering

國立宜蘭大學工程學刊第五期, 99-114頁, 2009年3月

Bulletin of College of Engineering, National Ilan University, NO. 5, P. 99-114, Mar.. 2009

# 回火對無定形聚對苯二甲酸乙二酯的影響

蔡宏斌<sup>1</sup> 李大剛<sup>2</sup> 蔡瑞禧<sup>3</sup> 方瀚宇<sup>4</sup>

1. 國立宜蘭大學化學工程與材料工程學系教授

- 2. 國立宜蘭大學化學工程與材料工程學系副教授
- 3. 大華技術學院化工與材料系副教授
- 4. 國立宜蘭大學化學工程與材料工程學系碩士班

### 摘 要

本文探討回火對無定形聚對苯二甲酸乙二酯(PET)板的影響。將原為無定形的 PET 板回火 可得不同結晶度的 PET 試片。回火的 PET 試片以示差掃描熱卡計(DSC),紫外線-可見光光譜儀 及 X 射線繞射儀分析描述之。在 80-100℃下回火 50 分鐘之後的 PET 試片仍維持無定形。而在 120℃或以上的溫度下回火 50 分鐘之後,PET 試片顯現明顯結晶。因此,在 110℃下將無定形 PET 板回火而得不同結晶度的 PET 試片。由 DSC 及可見光透過率數據可看出當回火溫度提高或 回火時間增長,PET 試片的結晶度有增高的趨勢。DSC 及可見光透過率數據亦顯示在 110℃下 回火超過 40 分鐘之後,PET 試片的結晶速率遠低於在 40 分鐘之內的結晶速率。

**關鍵詞:**聚對苯二甲酸乙二酯、結晶度、回火、熱性質、透光率。

# **1. INTRODUCTION**

Poly(ethylene terephthalate) (PET) is an important polymer material and widely used in fibers, films, bottles and plastics[Davis(1988), Goodman(1988), Jadhav(1988), Werner(1988)]. Poly(ethylene terephthalate) can be obtained as an amorphous solid by quenching from the melt. Poly(ethylene terephthalate) can also crystallize to a semi-crystalline material. The properties of poly(ethylene terephthalate) is strongly dependent on the crystallinity, and a lot of efforts have been made on this[Daniels(1958), Ellis(2000), Field-Russell(1970), Jabarin(1982), Johnson(1959), Khanna(1996), Khanna(1997), Li(2004), Lu(2002), Maruhashi(1992), Maruhashi(2001), Matthews(2004), Miyake(1959), Murthy(2003), Polyakova(2001), Rezaei(2005), Rwei(2000), Zumailan(2004)]. Typical properties under investigation include IR[Daniels(1958), Miyake(1959)], UV[Jabarin(1982)], X-ray diffraction[Field-Russell(1970), Johnson(1959), Murthy(2003)] and DSC[Field-Russell(1970), Khanna(1997)].

The crystallization of poly(ethylene terephthalate) is influenced by various factors such as molecular weight, catalyst system, comonomer content, nucleating agent and crystallization conditions[Khanna(1996)]. For example, orientation can cause stress-induced crystallization and influence the crystallinity[Ellis(2000), Khanna(1996), Maruhashi(1992), Maruhashi(2001), Zumailan(2004)]. The annealing of oriented poly(ethylene terephthalate) causes the polymer to crystallize, sometimes the process is called as heat setting. However, the crystallinity and the rate of crystallization are dependent on the crystallization temperature, and also on the amount of orientation in the amorphous phase[Khanna(1996)]. If amorphous poly(ethylene terephthalate) sheets without orientation are annealed, the effect of orientation can be excluded, and intrinsic relations between properties and the

crystallinity may be observed. In this article, amorphous poly(ethylene terephthalate) sheets were annealed to obtain samples of different crystallinity, and various properties were characterized.

# **2. EXPERIMENTAL**

Materials.

The amorphous PET sheet samples of 1 mm thickness, A-PET, were obtained from Nan Ya Plastics Corp. (Taiwan). The intrinsic viscosity was 0.70 dL/g.

The amorphous PET sheet samples were annealed by a program controllable HMO PC-900 high temperature oven (Fashing Inc., Taiwan). The amorphous PET sheet samples were heated in the oven from room temperature to an annealing temperature at a heating rate of 20°C/min, and held at that annealing temperature for various time intervals, afterwards, the sheet samples were cooled to room temperature without heating (a cooling rate of about 5°C/min). The chosen annealing temperatures were from 80 to 140°C, and the annealing time internals were from 10 to 1000 min.

The thermal properties of the annealed PET sheets from 50 to  $270^{\circ}$ C were determined by a Perkin Elmer DSC 7(differential scanning calorimeter) at a scanning rate of  $20^{\circ}$ C/min under nitrogen. The UV-visible spectra of the annealed PET sheets were determined by a Hitachi 2001 UV spectrophotometer at a scanning rate of 200nm/min. The X-ray diffraction patterns of annealed PET sheets were recorded by a Mac Science MXP-18 at a scanning rate of 4°/min.

# **3. RESULTS AND DISCUSSION**

The amorphous PET sheet samples were annealed at a temperature of 80-140  $^{\circ}$ C for 50 min. The PET sheet samples look transparent after annealing at 100 $^{\circ}$ C

(or below) for 50 min, and become opaque after annealing at  $120^{\circ}$ C (or above) for 50 min. The PET sheet samples annealed at  $110^{\circ}$ C for 50 min look translucent, thus an annealing temperature of  $110^{\circ}$ C was chosen for obtaining PET sheet samples of different crystallinity.

The first run DSC heating curves from 50 to  $270^{\circ}$ C of the PET sheet samples annealed at various temperatures for 50 min are shown in Figure 1. Within the annealing temperature range of 80 to  $100^{\circ}$ C, the first run DSC heating curves exhibit a step inflection corresponding to the glass transition, an exotherm corresponding to cold crystallization and an endotherm corresponding to melting. The mid-point of the step inflection is taken as the glass transition temperature (Tg), the peak temperature of the exotherm is taken as the cold crystallization temperature (T<sub>cc</sub>), and the peak temperature of endotherm is taken as the melting point(Tm). The first run DSC heating curves of the PET sheet samples annealed at 120-140 °C for 50 min exhibit different in that there is a small additional endotherm (denoted as TmL) instead of the cold crystallization exotherm. This TmL is just above the annealing temperature and can be described as a double melting behavior resulted from the formation of two different crystal populations. The thermal properties are summarized in Table 1.

Typical first run DSC heating curves of the PET sheet samples annealed at 110  $^{\circ}$ C for various time intervals are shown in Figure 2. As the annealing time increases, the area of the T<sub>cc</sub> decreases, and T<sub>cc</sub> disappears as the annealing time is over 100 min. As the annealing time is 100 min or longer, a T<sub>mL</sub> endotherm appears. The transition temperatures and the corresponding transition heats are summarized in Table 1. It can be seen from Figures 1, 2 and Table 1 that the crystallinity follows an increasing trend as the annealing temperature is raised for 50 min of annealing or as the annealing time increases at 110°C, as expected. It can be seen

103

Annealing	Annealing	Tg	T <sub>cc</sub>	$\Delta H_{cc}$	T <sub>mL</sub>	$\Delta H_{mL}$	T <sub>m</sub>	$\Delta H_{\rm m}$
temperature	time	(°C)	(°C)	(J/g)	(°C)	(J/g)	(°C)	(J/g)
Original	sample	76	142	-33.4			247	33.5
80°C	50 min	73	142	-33.7			246	33.6
100°C	50 min	71	135	-34.5			247	33.9
120°C	50 min	80			135	1.2	250	33.1
140°C	50 min	81			148	1.8	247	33.5
110°C	10 min	76	143	-33.3			246	32.3
110°C	20 min	73	137	-32.5			250	32.1
110°C	30 min	72	129	-30.1			247	33.6
110°C	40 min	73	128	-16.2			247	32.9
110°C	50 min	75	125	-6.2			246	32.4
110°C	100 min	78			121	1.0	246	32.7
110°C	200 min	77			124	1.6	245	32.9
110°C	500 min	83			128	1.9	249	33.2
110°C	1000 min	83			128	2.1	248	33.9

Table 1. Thermal properties of annealed PET sheet samples

from the  $\Delta H_{cc} + \Delta H_{mL} + \Delta H_m$  data in Table 1 that the change rate of the crystallinity, or the crystallization rate, at an annealing temperature of 110°C is strongly influenced by the annealing time. The crystallization rate after 40 min of annealing is significantly lower that before 40 min of annealing at 110°C.

It can also be seen from Figures 1, 2 and Table 1 that the lower melting endotherm  $(T_{mL})$  is affected by the annealing condition. In general, as the annealing temperature or the annealing time increase, both  $T_{mL}$  and  $\Delta H_{mL}$  increase as shown

in Table 1.

Typical UV/visible spectra of the annealed PET sheet samples are shown in Figures 3 and 4. The transmittance data at 500 and 800 nm are listed in Table 2. It can be seen that the transmittance in the visible region follows a decreasing trend as the annealing time increases at an annealing temperature of  $110^{\circ}$ C, or as the annealing temperature increases for an annealing time of 50 min due to the increase in the crystallinity, as expected. The trend is consistent with the DSC data.

It can be seen from Figures 3 and 4 that the loss in transmittance due to the increase in the crystallinity is different for different wave length in the visible region. For example, the transmittance at 500 nm decreases in a considerably faster rate than that at 800 nm as the crystallinity increases, initially. This might be due to the different size of crystallites which cause light scattering and lower the transmittance.

The transmittance curve of the sheet samples annealed at 100°C for 50 min shown in Figure 3 can be taken as an amorphous reference. The steep drop in transmittance below 400 nm is due to the absorption of UV light by the chromophores of PET molecules. The decrease in transmittance above 400 nm can be considered as an effect mainly caused by the light scattering the crystallites. The number, the volume fraction (related to the crystallinity), and the size of the crystallites contribute to the scattering of the light. As the crystallinity is very low, the size of the crystallites is small, and they scatter more light of shorter wave length. As the crystallinity increases, both the number and the size of the crystallites increase, the size effect of light scattering extends to longer wavelength. So the transmittance at longer wavelength decreases more slowly as the crystallites increases, at least for the sample of low crystallinity.

Annealing temperature	Annealing time	T <sub>500</sub> (%)	T <sub>800</sub> (%)	
80°C	50 min	84.6	87.4	
100°C	50 min	83.7	87.3	
120°C	50 min	0.5	14.4	
140°C	50 min	0.3	2.7	
110°C	10 min	85.1	88.2	
110°C	20 min	83.2	87.1	
110°C	30 min	34.4	64.8	
110°C	40 min	6.0	36.6	
110°C	50 min	3.8	35.8	
110°C	100 min	3.7	35.2	
110°C	200 min	3.3	34.8	
110°C	500 min	2.9	33.2	
110°C	1000 min	2.7	32.8	

Table 2. The transmittance at 500 and 800 nm of the annealed sheet samples

Although the dependence of light transmittance on the crystallinity is affected by the wavelength, the relationship is obvious at a given wavelength. The effect of annealing time at 110  $^{\circ}$ C on the change rate of the transmittance can be distinguished into two groups. As the annealing time at 110  $^{\circ}$ C is below 40 min, the change rate of the transmittance is rather fast. Taking the transmittance at 800 nm for comparison, the transmittance drops from 88.2% to 36.6% as the annealing time increases from 10 min to 40 min. As the annealing time at 110  $^{\circ}$ C is over 40 min, the change rate of the transmittance is very slow. The transmittance at 800 nm min. Thus, the crystallization rate after 40 min of annealing seems to be much lower that before 40 min of annealing at  $110^{\circ}$ C. The trend is consistent with the DSC data.

Typical X-ray diffraction patterns the annealed PET sheet samples are shown in Figure 5. The amorphous PET sheet samples such as that annealed at  $80^{\circ}$ C or  $100^{\circ}$ C for 50 min show no explicit diffraction peak. The PET sheet samples annealed at  $120^{\circ}$ C or  $140^{\circ}$ C for 50 min show obvious diffraction peaks. The diffraction peaks are at d spacings of 0.34, 0.39 and 0.52 nm, respectively. The PET sheet samples annealed at  $110^{\circ}$ C show interesting diffraction data. As the annealing time is 30 min or shorter, there is only a broad peak due to amorphous scattering, and no obvious diffraction peak has been observed. One possible reason is that the crystalline phase cannot behave continuously for these samples. It can be seen from Figure 5 that the wide angle X-ray diffraction analysis has limit signal to noise ratio, and some discrete crystalline domains might not be seen by the instrument. As the annealing time is 40 min or longer, sheet samples exhibit obvious diffraction peaks. It can be seen that the diffraction peaks show a tendency to be sharper as the crystallinity increases.

#### 4. CONCLUSION

The PET sheet samples annealed at 80 or  $100^{\circ}$ C for 50 min remain amorphous. But the PET sheets annealed at  $120^{\circ}$ C or above for 50 min show significant crystallization. Thus, an annealing temperature of  $110^{\circ}$ C has been chosen for obtaining PET sheet samples of different crystallinity. It can be seem that as the annealing temperature or time increases, the crystallinity follows an increasing trend. The DSC and light transmittance data show that the crystallization rate after 40 min of annealing is much lower that before 40 min of annealing at 110  $^{\circ}$ C. Thus, it is easier to obtain PET sheet samples of significantly different crystallinity by annealing at 110 $^{\circ}$ C within 40 min.

### Acknowledgement

The authors thank the National Science Council of the Republic of China for the financial support of this work under the grant no. of NSC 94-2622-E-197-006-CC3.

## REFERENCES

- Daniels, W. W. and Kitson, R. E. (1958), "Infra Spectroscopy of Polyethylene Terephthalate", J. Polym. Sci., Vol. 33, pp. 161-170.
- Davis, G. W. and Talbot, J. R. (1988), "Polyesters, Elastomeric", *Encyclopedia of Polymer Science and Engineering (Mark, H. F., Bikales, N. M., Overberger, C. G, Menges, G. and Kroschwits, J. I. Eds.), 2nd Ed.*, Vol. 12, pp. 118-193, Wiley, New York.
- 3. Ellis, J. W. and Picot, J. J. C. (2000), "Mechanical and Thermal Anisotropy for Uniaxially and Biaxially Draw PET", *Polym. Eng. Sci.*, Vol. 40, 1619-1627.
- Field-Russell, G. S. and Padmanabha, S. P. (1970), "A Study of the Crystallization of Polyethylene Terephthalate Using Differential Scanning Calorimetry and X-ray Techniqus", *Makromol. Chem.* Vol, 135, pp. 263-274.
- Goodman, I. (1988), "Polyesters", Encyclopedia of Polymer Science and Engineering (Mark, H. F., Bikales, N. M., Overberger, C. G., Menges, G. and Kroschwits, J. I. Eds.), 2nd Ed., Vol. 12, pp. 1-75, Wiley, New York.
- 6. Jabarin, S. A. (1982), "Optical Properties of Thermally Crystallized Poly(ethylene Terephthalate)", *Polym. Eng. Sci.*, Vol. 22, pp. 815-820.
- 7. Jadhav, J. Y. and Kantor, S. W. (1988), "Polyesters, Films", Encyclopedia of

Polymer Science and Engineering (Mark, H. F., Bikales, N. M., Overberger, C.G., Menges, G. and Kroschwits, J. I. Eds.), 2nd Ed., Vol. 12, pp. 217-256, Wiley,New York, 1988.

- Johnson, J. E. (1959), "X-ray Diffraction Studies of the Crystallinity in Polyethylene Terephthalate", *J. Appl. Polym. Sci.* Vol, 2, pp. 205-209.
- Khanna, Y. P. and Kuhn, W. P.(1996), "Polyethylene Terephthalate (Heat-setting and Thermal Stabilization), *Polymeric Materials Encyclopedia* (*Salamone, J. C. Ed.*), Vol. 8, pp. 6091-6100, CRC Press, New York.
- Khanna, Y. P. and Kuhn, W. P. (1997), "Measurement of Crystalline Index in Nylons by DSC: Complexities and Recommendations", *J. Polym. Sci. Part B: Polym. Phys.*, Vol. 35, pp. 2219-2231.
- 11. Li, Z. M., Xie, B. H., Huang, R., Fang, X. P. and Yang, M. B. (2004),
  "Influence of Hot Strecth Ratio on Essential Work of Fracture of in-situ Microfibrillar Poly(ethylene Terephthalate)/Polyethylene Blends", *Polym. Eng. Sci.*, Vol. 44, pp. 2165-2173.
- Lu, W., Debelak, K. A., Witt, A. R., Yang, C., Collins, W. E. and Lott, C. (2002), "Structure Features of Crystallized Poly(ethylene Terephthalate) Polymers", *J. Polym. Sci. Part B: Polym. Phys.*, Vol. 40, pp. 245-254.
- Maruhashi, Y. and Asada, T. (1992), "Structure and Physical Properties of Biaxially Stretched Polyethylene Terephthalate Sheet after Heat-setting", *Polym. Eng. Sci.*, Vol. 32, pp. 481-487.
- Maruhashi, Y. (2001), "Structure and Physical Properties of Biaxially Stretched Polyethylene Terephthalate Sheet under Different Heat-set and Stretch Conditions", *Polym. Eng. Sci.*, Vol. 41, pp. 2194-2199.
- 15. Matthews, S. R., Hwang, Y. J., McCord, M. G. and Bourham, M. A. (2004), "Investigation into Etching Mechanism of Polyethylene Terephthalate (PET)

Films Treated in Helium and Oxygenated-helium Atmospheric Plasmas", *J. Appl. Polym. Sci.*, Vol. 94, pp. 2383-2389.

- Miyake, A. (1959), "The Infrared Spectrum of Polyethylene Terephthalate. I The Effect of Crystallization", *J. Polym. Sci.* Vol. 34, pp. 479-495
- Murthy, N. S. and Grubb, D. T. (2003), "Deformation in Lamellar and Crystalline Structures: In situ Simultaneous Small-angle X-ray Scattering and Wide-angle X-ray Diffraction Measurements on Polyethylene Terephthalate Fibers", *J. Polym. Sci. Part B: Polym. Phys.* Vol. 41, pp. 1538-1553.
- Polyakova, A., Stepanov, E. V., Sekelik, D., Schiraldi, D. A., Hiltner, A. and Baer, E. (2001), "Effect of Crystallization on Oxygen-barrier Properties of Copolyesters Based on Ethylene Terephthalate", *J. Polym. Sci. Part B: Polym. Phys.*, Vol. 39, pp. 1911-1919.
- Rezaei, M., Ebrahimi, N. G. and Kontopoulou, M. (2005), "hermal Properties, Rheology and Sintering of Ultra High Molecular Weight Polyethylene and Its Composites with Polyethylene Terephthalate", *Polym. Eng. Sci.*, Vol. 45, pp. 678-686.
- 20. Rwei, S. P. (2000), "Modification of PET in High-speed Melt Spinning by Blending with PEN", *Polym. Eng. Sci.*, Vol. 40, pp. 191-200.
- Werner, E., Janocha, S., Hopper, M. J. and Mackenzie, K. J. I. (1988),
   "Polyesters, Fibers", *Encyclopedia of Polymer Science and Engineering* (*Mark, H. F., Bikales, N. M., Overberger, C. G., Menges, G. and Kroschwits, J. I. Eds.*), 2nd Ed., Vol. 12, pp. 193-216, Wiley, New York.
- 22. Zumailan, A., Dargent, E, and Saiter, J. M. (2004), "Characterization of Polyethylene Terephthalate Films Drawn in Hot Water", *Polym. Eng. Sci.*, Vol. 44, pp. 223-230.



Figure 1. First run DSC heating curves of the PET sheet samples annealed at various temperatures for 50 min.



Figure 2. First run DSC heating curves of the PET sheet samples annealed at  $110^{\circ}$ C for various time intervals.



Figure 3. UV/visible spectra of the PET sheet samples annealed at various temperatures for 50 min.



Figure 4. Typical UV/visible spectra of the PET sheet samples annealed at  $110^{\circ}$ C for various time intervals.



Figure 5. Typical X-ray diffraction patterns of annealed PET sheet samples.