Journal of Thermal Analysis, Vol. 52 (1998) 565-568

PLASTICIZATION AND CRYSTALLIZATION OF POLY(ETHYLENE TEREPHTHALATE) INDUCED BY WATER

Y. Chen, Z. Lin and S. Yang

Zhongshan University, Institute of Polymer Science, Guangzhou, P.R. of China

Abstract

Commercial poly(ethylene terephthalate) (PET) was treated at R. H.>80% and room temperature for a set time. The glass transition temperature (T_g) decreases with the time of exposure to high humidity. The decrease in T_g is a result of plasticization. Our data indicate that the T_g of dry PET of 76–78°C may decrease to as low a temperature as 65–67°C when it is wet. Induced crystallization of PET in the presence of water reduces the cold crystallization temperature (T_c). The structure of water-induced crystals is imperfect and can be improved in perfection by annealing.

Keywords: plasticization effect of water, poly(ethylene terephthalate), water-induced crystallization

Introduction

The commercial application of poly(ethylene terephthalate) resin, PET, is unlimited in fibers, in films, bottles, engineering plastics, etc. Plasticization and crystallization of PET are often used in demonstrative discussions, but plasticization and crystallization induced by water are noticed by us with double peaks during the cold crystallization of PET [1, 2]. In this paper water-induced events are in the focus.

Experiment

Sample

The sample used in the study is commercial PET resin.

PET was placed in the crucible of the DSC apparatus. The effect of the thermal history of the PET sample was eliminated by melting at 290–300°C for 10 min, and subsequent quenching in an ice bath (the sample must not come into contact with water). The sample thus prepared was treated at R. H.>80% and room temperature for a set time.

1418-2874/98/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

Differential Scanning Calorimetry (DSC)

All DSC experiments were performed on a Shang-Hai CDR-1 differential scanning calorimetry at a heating rate of 10°C min^{-1}.

Results and discussion

Plasticization of PET by water

In Fig. 1 the glass transition temperature (T_g) is shown to decrease with increasing treatment time. The water content was determined by weighing the difference between dry and wet PET. At the same time the water content of the sample rises from 0.25% in 15 h to 0.63% in 100 h, Fig. 2. It is well known that the decrease in T_g is the result of plasticization. Hydrogen bonds are formed between water molecules and polar ester groups, so that the number of interchain hydrogen bonds is reduced, allowing main chain relaxation to become easier.

The T_g of PET is usually between 65–78°C. The main reason for the difference in T_g is the difference in water content except the method of determination. Our study indicates that the T_g of dry quenched PET is 76–78°C and the T_g of wet quenched PET is 65–67°C. The dry PET will be plasticized after it sucks up moisture. It causes the T_g of PET to decrease.

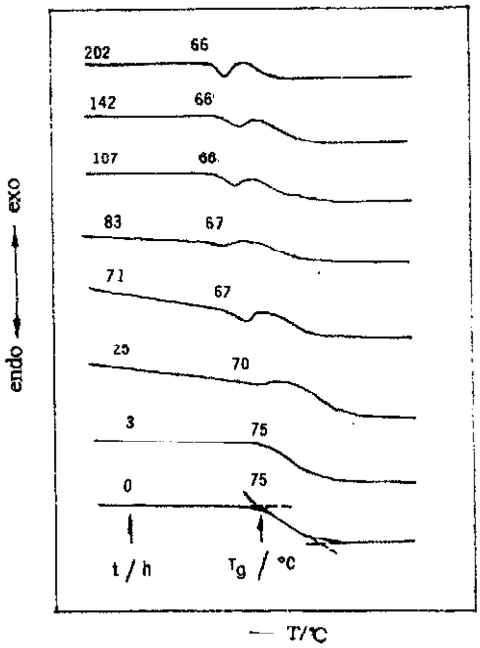

Fig. 1 T_g of PET *vs.* time of exposure (room temperature. R.H.=84·10^{-2})

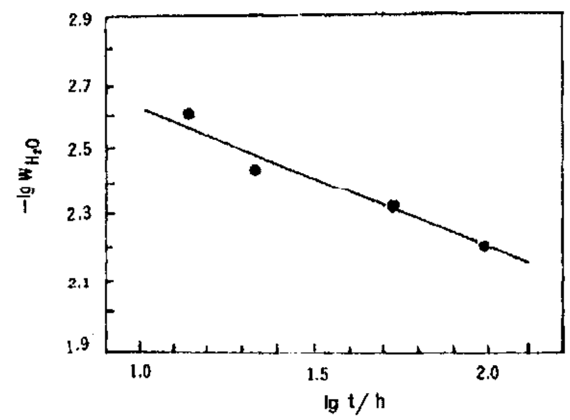

Fig. 2 Water content of the PET sample *vs.* time of exposure

Crystallization of PET induced by water

Water is a polymer plasticizer, so that induced crystallization of PET by water can cause a decrease in the cold crystallization temperature (T_c). Some experimental results are shown in Fig. 3, the T_g values of PET samples from a Shang Hai source and a Japanese source, may be lowered by as much as 25°C by exposure to high humidity.

In Table 1 are listed changes caused by annealing treatment in the characteristic parameters of PET plasticized by water. T_m is the melting endothermic peak temperature determined by DSC for the crystal which was formed during

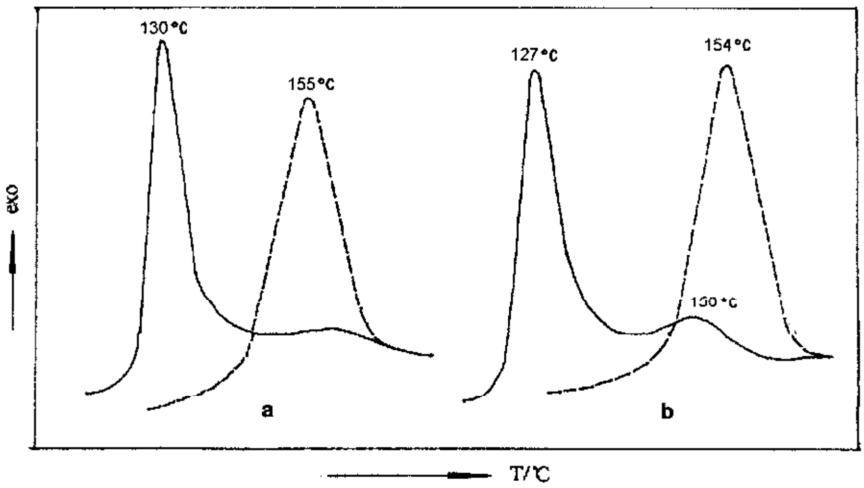

Fig. 3 Cold crystallization of PET samples (DSC method) --- dry PET: — wet PET. Sample from: a – Shanghai; b – Japan

Table 1 Changes in the characteristic parameters of PET samples with treatment time and temperature

Treatment T/°C	Condition t/h	T_m/°C	Crystallinity/%		C^*/%
			X_d	X_x	
120	1.5	142	31.15	25.2	70.1
120	4.5	142	30.77	19.2	69.9
120	6.0	142	30.77	25.2	70.2
150	1.0	165		30.4	73.5
150	3.0	167			
150	4.5	170	30.92	30.92	76.7
150	6.0	172	30.72	30.8	78.1

C^* – crystallinity index

annealing. X_d is the crystallinity determined by the density method. X_x is the crystallinity determined by the WAXS method. C is the crystallinity index. It can express the degree of perfection of the crystal. The consequence of annealing at higher temperature (higher than the cold crystallization peak temperature e.g., at 150°C) is an increase in the melting point. The crystallinity index increases linearly with annealing time while the crystallinity does not change [3]. These results indicate that the structure of water-induced crystals is imperfect and can be improved by annealing.

Reference

1 Yang Shikun, Chen Xiangming, Chen Yujun, Polymer communications, 3 (1985) 207.
2 Yang Shikun, Liu Yu, Chen Yujun et al., Hecheng Xianwei Gongye, 1 (1985) 15.
3 Yang Shikun, Li Shaohua, Pan Jianyuan, Sup. to the Acta Sci. Naturelium Universitatis Sunyatseni, 3 (1990) 8.