

EFFECT OF CHEMICAL STRUCTURE OF COMONOMERS ON THE PROPERTIES OF COPOLYESTERS

WU Rongrui (武荣瑞) GAO Jing (高 谨) and LI Huiping (李慧萍)

(Academy of Synthetic Fiber, Beijing Institute of Clothing Technology, Beijing 100029)

ABSTRACT

The effect of different kinds of comonomers with or without flexible chain on properties of copolyesters, such as transition temperature, crystallization velocity, crystallinity and size of crystallites, is studied. The experimental results indicate the obvious difference in properties between comonomers with iso- and ortho-structure of phenyl ring and comonomers with flexible chain. The influence of chemical structure of comonomers on properties of copolyesters is discussed.

INTRODUCTION

Several works related to the preparation and properties of copolyesters have been published^[1-3]. A more important problem, however, is the influence of chemical structure of comonomers on the properties of resulted copolymers. But there is relatively few publications on this subject for polyethyleneterephthalate (PET) copolymers. In this paper the effect of different kinds of monomers with or without flexible chain on properties of polyethyleneterephthalate copolyesters will be discussed.

EXPERIMENTAL

The monomers used are as follows: Dimethyl terephthalate (DMT), terephthalic acid (TPA), isophthalic acid (IPA), 5-sulphodimethyl-1-isophthalate (SIPM), dimethyl-orthophthalate (DMO), dimethyl sebacate (DMS), polyethyleneglycol (PEG). The copolymers were obtained by two methods: (1) direct esterification of TPA and IPA with ethyleneglycol (EG) (under 0.33 MPa, without catalysts) and

then followed by melt polycondensation (280°C, 40 pa, with trioxantimony as catalyst). (2) esterexchange reaction of DMT and monomers (SIPM, SIPM+DMO, SIPM+DMS) with EG (catalysts were cobalt acetate and calcium acetate) and then followed by melt polycondensation (280°C, 40 pa, trioxantimony was used as catalyst). PEG was added before polycondensation.

Transition temperature of copolyesters was determined by Perkin Elmer differential scanning calorimeter DSC-2.

Crystallization velocity was determined by apparatus with dispelled polarized light JJY-1A (made in Yin Kou Testing Instrument Factory, China).

X-ray analysis was accomplished by Wide Angle X-ray Diffractionmeter D/max-rB.

RESULTS AND DISCUSSION

The kinds of additive comonomers are shown in Table 1.

Table 1 Comonomers added

Esterification method (mol% to TPA)	Esterexchange method (mol% to DMT)
* IPA	* SIPM
	* SIPM (2 mol%) + DMO
* PEG (added in polycondensation)	* SIPM (2 mol%) + DMS
	* SIPM (2 mol%) + PEG (added in polycondensation)

1. Glass transition temperature and melting point

The glass transition temperature T_g and melting point T_m of different copolyesters are shown in Figs. 1, 2 and 3.

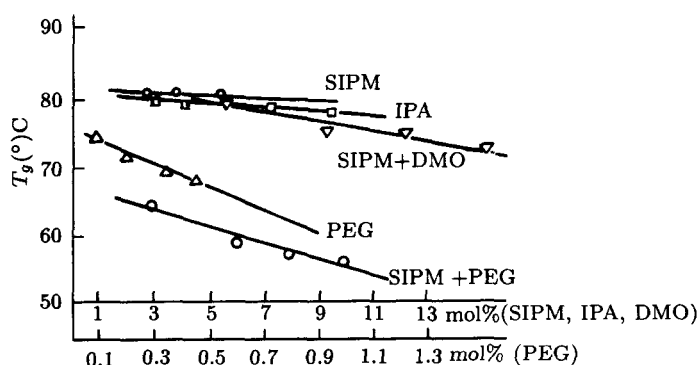


Fig. 1 T_g of PET copolyesters

Comonomers: SIPM, IPA, SIPM (2 mol%) + DMO, PEG, SIPM (2 mol%) + PEG

It is well known that T_g increases with the increase of crystallinity and degree of orientation of fiber in the process of stretching and heat setting, so the decrease of T_g of polymer by copolycondensation modification is advantageous for fiber dyeing and moisture absorption. It is shown in Fig. 1, when a copolycondensation component with flexible chain is introduced into the macromolecules the T_g of the obtained copolymer decreases obviously.

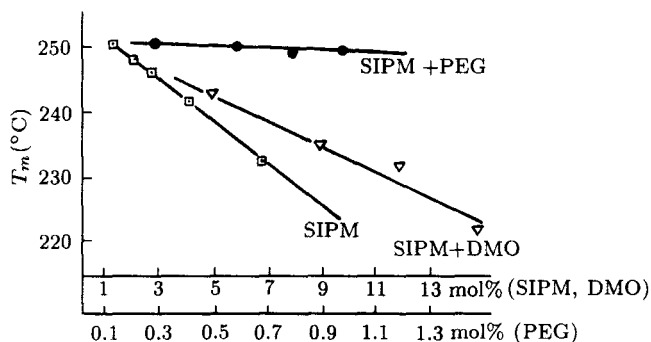


Fig. 2 T_m of PET copolyesters

Comonomers: SIPM, SIPM (2 mol%) + DMO, SIPM (2 mol%) + PEG

The melting points T_m of obtained copolyesters are shown in Figs. 2 and 3. The addition of copolycondensation components leads to the disturbance of the regular structure of PET, so the T_m of all copolyesters are decreased ($T_m = \Delta H/\Delta S$). But when the added component is PEG, the T_m is changed insignificantly. Because T_m of this copolymer is dependent on the molal percent of PEG component^[4]. In our experimental work a small molal percent of PEG was used.

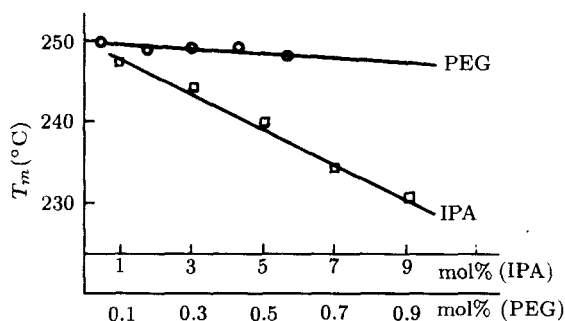


Fig. 3 T_m of PET copolyesters

Comonomers: IPA, PEG

2. Cold crystallization temperature and crystallization velocity

Cold crystallization temperature and crystallization velocity are important parameters for improving shrinkage property of polyester fibres.

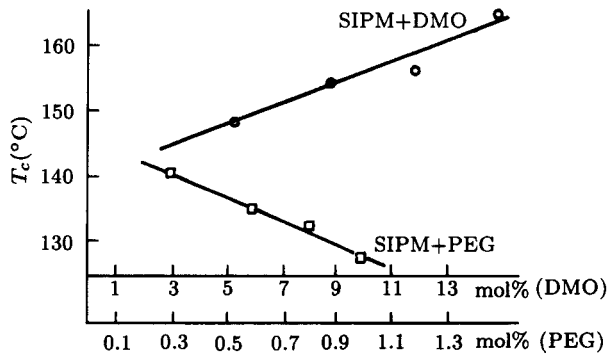


Fig. 4 T_c of PET copolyesters
Comonomers: SIPM (2 mol%) +DMO, SIPM (2 mol%)+PEG

The data of cold crystallization temperature T_c are shown in Fig. 4 and crystallization velocity V_c in Fig. 5 and Fig. 6, respectively. Introduction of iso- and ortho-structure of phenyl ring leads to an increase of T_c . On the contrary, introduction of long flexible chain of PEG leads to a decrease of T_c of this copolymer. Results of determination of crystallization velocity V_c of copolyesters show a good agreement with the obtained data of T_c (Fig. 5, Fig. 6).

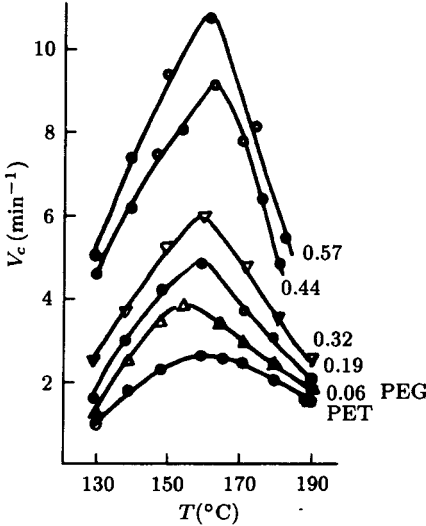


Fig. 5 V_c of PET copolyesters
Copolycondensation component: PEG (4000)

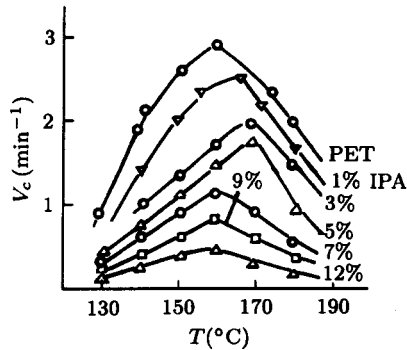


Fig. 6 V_c of PET copolyesters
Copolycondensation component: IPA

3. Crystallinity and crystallite size

The crystallinity X% and crystallite size in nm of copolyesters determined by X ray analysis are shown in Table 2.

Table 2 Crystallinity and crystallite size of copolyesters

Comonomer	Mol % to TPA or DMT	Crystallinity X%	Crystallite size (nm)	
			D_{T00}	D_{TT3}
PET	—	62.9	2.89	1.43
IPA	3.00 (TPA)	56.0	3.07	—
	5.00	55.5	3.24	—
PEG (4000)	0.19 (TPA)	58.5	2.86	—
	0.32	59.6	2.89	—
SIPM	1.30 (DMT)	56.0	2.81	1.69
	2.60	54.8	2.98	1.95
SIPM+	2.00 (DMT)			
DMO	8.93	52.0	2.91	2.07
	14.80	51.7	3.08	2.40
SIMP +	2.00 (DMT)			
PEG (2000)	0.29	57.9	2.76	1.68
	0.59	54.3	2.84	2.34

The crystallinity of copolyesters having iso- and ortho- phenyl ring decreased more significant than that of copolyesters with the flexible PEG chain. These results are in agreement with the obtained data of V_c and T_c . In comparison with homopolymer PET the crystallite size of copolymers increases and this increase is enhanced with increasing of the quantities of additive components. Increasing of crystallite sizes of copolymers is advantageous for improving the dyeing properties of polyester fibers.

Keywords:

Copolyesters; Polyethyleneterephthalate; Comonomer; Chemical structure

REFERENCES

- [1] Wu, R.R. and Shi, W.T., *Chinese J. Polym. Sci.*, **1992**, 10(4): 356.
- [2] Wu, R.R.; Huang, G.B.; Xie, B.Y.; Deng, Y. and Zhang, Y.L., *Acta Polymerica Sinica*, (in Chinese) **1993**, (2): 252.
- [3] Wu, R.R.; Deng, Y.; Huang, G.B.; Deng, J.Y. and Li, H.P., *Chinese J. Polym. Sci.*, **1994**, 12(1): 80.
- [4] Luigi, Sieo, *Advances in Polymer Science*, **1979**, 31: 89.