

THERMAL PROPERTIES OF MECDP COPOLYESTERS

by

**Ming-Liang ZHAO^a, Yuan LIU^a, Fa-Xue LI^{a*}, Xue-Li WANG^b,
Yu GAO^b, and Jian-Yong YU^{b*}**

^a College of Textile, Donghua University, Shanghai, China

^b Modern Textile Institute, Donghua University, Shanghai, China

Short paper

DOI: 10.2298/TSCI1205456Z

MECDP copolyesters based on poly(ethylene terephthalate) were prepared with sodium-5-sulfo-bis-(hydroxyethyl)-isophthalate and poly(ethylene glycol) units as modifiers. Thermal properties of these copolyesters were characterized by differential scanning calorimetry and thermal gravity analyzer. Experimental results indicated that glass transition temperature, melting temperature and thermal degradation temperature reduced with increasing the poly(ethylene glycol) content. The incorporation of poly(ethylene glycol) increased the flexibility and irregularity of molecular chains which led to lower crystallinity, and brought more ether bonds into molecular chains. Besides, the thermal degradation under oxygen condition happened easily compared to that under nitrogen condition.

Key words: MECDP, thermal properties, differential scanning calorimetry, thermal gravity analyzer

Introduction

Poly(ethylene terephthalate) (PET) is widely used due to its superior properties. However, the disadvantages of PET fiber are hindering its use in textile and apparel industry. The cationic dyeable polyester (CDP), owning negative dye site (sulfonated group), was successfully prepared in 1960s. CDP fibers can be dyed into bright and lively colors with cationic dyes [1], but high temperature and pressure condition is necessary. Based on CDP, easy cationic dyeable polyester (ECDP) has been synthesized by incorporating poly(ethylene glycol) (PEG) into CDP. However, thermal properties were affected if the molecular weight of the incorporated PEG units is too low [2].

Many papers reported the properties of PET modified with PEG ($M_n = 2000-4000$), but to the best of our knowledge, no previous research has discussed the influence of PEG with high molecule weight on PET. Herein, we reported the thermal properties of the PET-based copolyesters modified with PEG ($M_n = 6000$) (abbreviated as PEG6000) and sodium-5-sulfo-bis-(hydroxyethyl)-isophthalate (SIPE).

Experimental

MECDP samples were successfully synthesized with direct esterification method. For all samples, the feed molar ratio of SIPE to PTA was set to 3:100, while the feed weight

* Corresponding author; e-mail: fxlee@dhu.edu.cn, or yujy@dhu.edu.cn

ratio of PEG6000 to PTA was varied for 0/100, 1.5/100, 3/100, 5/100, 10/100, 15/100 named as MECDP0, MECDP1.5, MECDP3, MECDP5, MECDP10 and MECDP15.

Differential scanning calorimetry (DSC) measurement was performed by NETZSCH DSC204F1. The sample was heated from 20 °C to 290 °C at the rate of 20 °C per minute. Thermal gravity analyzer (TGA) measurement was executed by NETZSCH TGA209F1 under oxygen and nitrogen atmosphere, respectively. The sample was gradually heated from 25 °C to 600 °C at the rate of 10 °C per minute.

Results and discussion

DSC analysis

Figure 1 shows the DSC heating curves of MECDP samples, and thermal parameters were listed in tab. 1. The glass transition temperature T_g was found to gradually decrease when the feed amount of flexible PEG6000 units increased. This suggested that the flexibility and irregularity of the molecular chains enhanced, and the free volume and amorphous regions of copolyesters increased. Consequently, less energy was needed to make molecular chain segments moving. Generally, as T_g became lower, the sample was endowed better flexibility and soft handling.

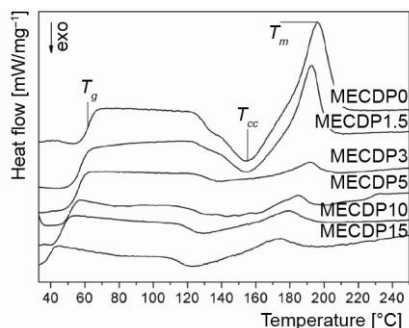


Table 1. The values of T_g , T_{cc} , and T_m of MECDP samples

Sample	T_g [°C]	T_{cc} [°C]	T_m [°C]
MECDP0	61.3	155.1	196.2
MECDP1.5	58.2	154.5	193.9
MECDP3	56.9	142.5	191.4
MECDP5	51.6	141.7	185.2
MECDP10	46.1	129.4	179.5
MECDP15	40.1	123.5	174.7

Figure 1. DSC curves of MECDP samples

The cold-crystallization temperature (T_{cc}) of all samples gradually reduced when the content of PEG6000 units increased. This indicated that the sample tended to crystallize at lower temperature with the increasing quantity of PEG6000 units. However, the lower temperature for sample crystallization caused the worse motion ability of molecular chains. Therefore, it is easy to form more defective crystals [3].

The melting temperature T_m was found to gradually depress when the feed amount of PEG6000 units increased. Since the incorporation of PEG6000 brought more ether bonds(-o-) into molecular chains, the reduced regularity of molecular chains led to more amorphous regions, lower degree of crystallinity and defective crystalline structure [4]. These defective crystals would be destroyed at lower temperature.

TGA discussion

Figures 2 and 3 present the TGA and dTGA curves of MECDP samples under nitrogen and oxygen atmospheres. It could be seen that the TGA curves shifted to left side with in-

creasing the PEG6000 content, meaning that the thermal stability became worse. The thermal degradation temperatures T_d correspond to different weight losses were summarized in tab. 2.

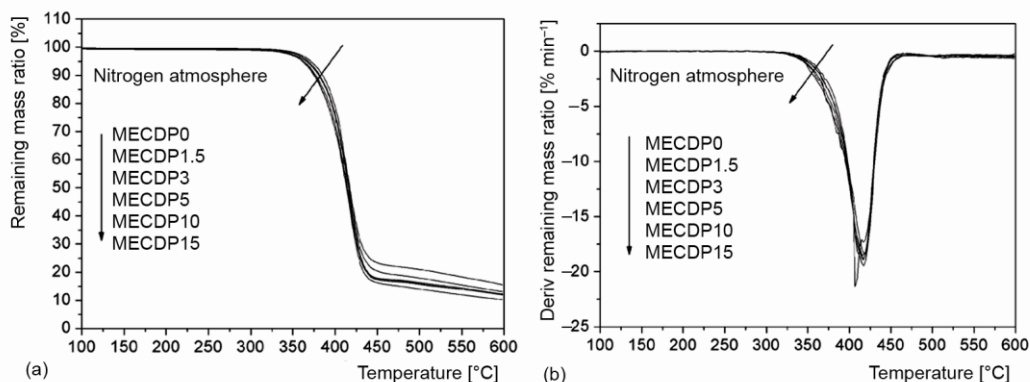


Figure 2. TGA(a) and dTGA(b) curves of MECDP samples under nitrogen atmosphere

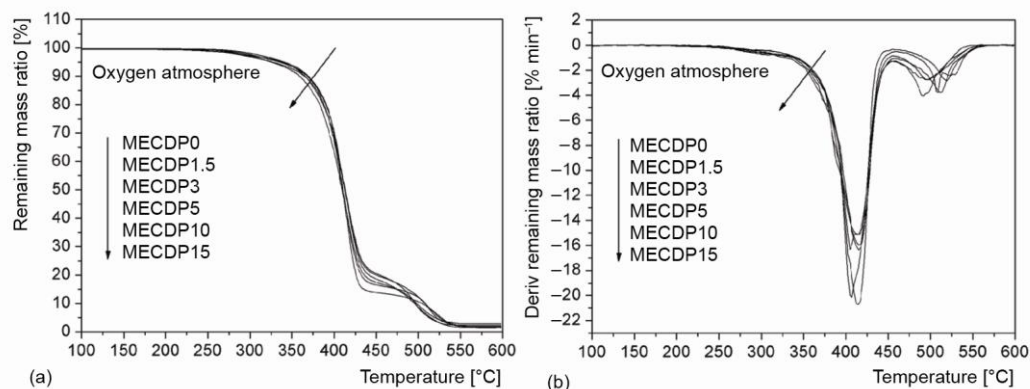


Figure 3. TGA(a) and dTGA(b) curves of MECDP samples under oxygen atmosphere

Table 2. The degradation temperatures of MECDP samples at different weight losses

Sample	T_d under nitrogen atmosphere (°C)			T_d under oxygen atmosphere (°C)		
	Onset	30%	50%	Onset	30%	50%
MECDP0	394.9	406.6	417.3	387.7	400.3	413.1
MECDP1.5	391.6	405.2	415.6	386.9	399.7	410.5
MECDP3	390.4	404.8	414.9	386.1	397.9	410
MECDP5	389.1	402	414.3	385.9	397.1	409.6
MECDP10	388.6	400.5	413.5	384.8	396	408.8
MECDP15	387.9	399.3	412.6	381.2	394.1	407.9

When more PEG6000 units were incorporated into molecular chains, more ether bonds were blocked into the molecular bones. Ether bonds enhanced the electronegativity of oxygen atom in the ester carbonyl, and increased the electropositivity of hydrogen atom in the

methylene [5]. Therefore, it was more prone to rupture for relative bonds in copolyesters and then produced new free radicals and end groups, which led to the easier thermal degradation.

Moreover, it was also found that there was one weight-loss stage of dTGA curves under nitrogen atmosphere, while two weight-loss stages appear under oxygen atmosphere. The first weight-loss stage was mainly attributed to the thermal degradation process of long molecular chains into shorter molecular chain fragments when samples were heated up to certain high temperature [6]. Subsequently, these fragments were thermal-oxidized into smaller residues because of the existence of oxygen, which resulted in the appearance of the second weight-loss stage [7].

Conclusions

Thermal properties of MECDP samples were probed by DSC and TGA. When the feed amount of flexible PEG6000 units increased, the T_g , T_{cc} , T_m , and T_d of MECDP samples were reduced. The incorporation of PEG6000 led to more amorphous regions, more defective crystalline structure and lower crystallinity. Meanwhile, the more ether bonds into molecular chains enhanced the electronegativity of oxygen atom in the ester carbonyl and increased the electropositivity of hydrogen atom. So the hydroxyl and carboxyl end groups and free radicals were formed to induce the thermal degradation.

Acknowledgement

This work is supported by National "Twelfth Five-Year" Science and Technology Support Program of China: The Key Manufacturing Technique Development of New Polyester Cotton-like Fibers (No.2011BAE05B04), and the Fundamental Research Funds for the Central Universities (No.12D10143).

References

- [1] Lee, M. S., *et al.*, Ozone-Gas Treatment of Cationic Dyeable Polyester and PET Fibers, *Journal of Applied Polymer Science*, 104 (2007), 4, pp. 2423-2429
- [2] Hsiao, K. J., *et al.*, Physics and Kinetics of Alkaline Hydrolysis of Cationic Dyeable Poly(Ethylene Terephthalate) (CDPET) and Polyethylene Glycol (PEG)-Modified CDPET Polymers, *Journal of Applied Polymer Science*, 98 (2005), 2, pp. 550-556
- [3] Varma, D. S., *et al.*, Poly(Ester-Ether) Fibres. *Die Angewandte Makromolekulare Chemie*, 52 (1980), 1, pp. 23-36
- [4] Kiyotsukuri, T., *et al.*, Poly(Ethylene-Terephthalate) Copolymers with a Smaller Amount of Poly(Ethylene Glycol)s and Poly(Butylene Glycol)s. *Polymer*, 36 (1995), 13, pp. 2629-2635
- [5] Wei, G. F., Hua, D. B., Gu, L. X., Thermal Stability of Poly(Ethylene-Co-Trimethylene Terephthalate)s, *Journal of Applied Polymer Science*, 101 (2006), 5, pp. 3334-3335
- [6] Li, X. G., Huang, M. R., Bai, H., Kinetics of Thermal Degradation of Liquid-Crystalline Aromatic Polymers, *Die Angewandte Makromolekulare Chemie*, 256 (1998), 1, pp. 9-19
- [7] Li, F. X., *et al.*, Thermal Degradation and their Kinetics of Biodegradable Poly(Butylene Succinate-Co-Butylene Terephthalate)s under Nitrogen and Air Atmospheres, *Polymer Degradation and Stability*, 91 (2006), 8, pp. 1688-1693

Paper submitted: July 15, 2012

Paper revised: August 22, 2012

Paper accepted: August 24, 2012