

STUDY ON SOME PROPERTIES OF SI-CONTAINING POLYESTER-POLYETHER MULTIBLOCK COPOLYMERS

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ABSTRACT

Some physical properties of the polyester-polyether multiblock copolymers with Si-containing hard segment were further examined by a series of physical methods. The hydrophobicity of the copolymers was improved with the incorporation of increasing amount of organosilicone, XPS test proved that silicon element was enriched at the surface of the Si-containing polyester-polyether copolymers. It was also found that their heat resistance and gas permeability for O₂ and N₂ were greatly improved. The study on semipermeability of films made of the Si-containing copolymers was also followed with interest.

INTRODUCTION

In recent years, it has been reported that the incorporation of organosilicone compounds can greatly improve the properties of polyester-polyether multiblock copolymers such as antistatic properties^[1,2] and abrasion resistance^[3]. Even the Si-containing polyester-polyether could be used as surgical threads^[4]. Modification of polyester-polyether multiblock copolymers with organosilicone had been reported only on the alteration of soft segment^[5]. In our previous work^[6], the polyester-polyether multiblock copolymers with Si-containing in hard segment have been synthesized and characterized. This paper further examined some physical properties of the synthesized Si-containing copolymers.

EXPERIMENTAL

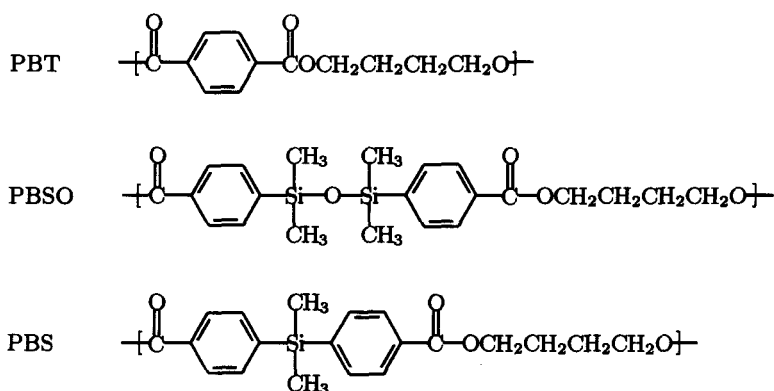
1. Synthesis

The synthesis of the Si-containing polyester-polyether copolymers was reported in our previous paper^[6]. The organosilicone compounds were introduced into the

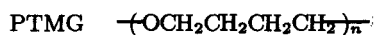
hard segments of the copolymers. In other words, the polybutylene glycol terephthalate (PBT) and organosilicone monomers formed a random copolymerized hard segments of the Si-containing copolymers. The soft segments of these copolymers, however, were identical, i.e. polytetramethylene glycol (PTMG) with a molecular weight of 1000.

The hard segment and soft segment structures of these copolymers were shown in Scheme 1. The segment compositions and intrinsic viscosity $[\eta]$ of the copolymers are given in Table 1.

Hard segment:



Soft segment:



where $n = 14$

Scheme 1

Table 1 Segment compositions* and intrinsic viscosity of copolymers synthesized

Copolymers	Hard segment (wt%)	Soft segment (wt%)	Si-segment content in hard segment		$[\eta]$
			PBSO	PBS	
PBT-PTMG [I]	31.1	68.9			1.37 1.28
(PBT-co-PBSO-)-PTMG [II]	30	70	6.0		1.26 1.47
(PBT-co-PBSO-)-PTMG [III]	30	70	12.5		1.47
(PBT-co-PBS-)-PTMG [IV]	34	66		5.6	
(PBT-co-PBS-)-PTMG [V]	34.5	65.5		12.5	

* Segment compositions were calculated from $^1\text{H-NMR}$ data

2. Contact angle and XPS

The 3 wt% dilute solution of these copolymers in CHCl_3 was continually dropped onto a microscope slide until the whole slide was covered with the solution, and the

solvent was slowly evaporated at room temperature, then dried in a vacuum oven at 50°C for 8 h. The contact angle of the film to water was measured by a CA-D type contact anglemeter (Lyowa Kaimenkagaku Co.). The results were an average of 4 measured values. XPS data for the amount of C, Si at different depth were obtained on a KEATOS ES-300 Photoelectron Spectroscopy using the thin film peeled off from the above microscope slide as sample.

3. *Film preparation*

All the films of above copolymers for mechanical measurement and gas permeability determination were made by the following procedure: 8 g copolymer, which was purified by reprecipitation using CHCl_3 as solvent and CH_3OH as precipitant before use, was dissolved in 100 ml CHCl_3 . Films were obtained by casting the solution on the glass plate and the solvent was slowly evaporated at room temperature. The films formed were peeled off and dried under vacuum at 50°C for 8 h.

4. *Gas permeability and heating weight loss determination*

Gas permeability of the copolymer films for N_2 and O_2 was measured on G.T.R.K-310-N type instrument. The heating weight loss determination was carried out on a heating weight loss balance.

5. *Differential scanning calorimeter (DSC)*

Before DSC analysis the samples of copolymers were heated to 100°C and annealed for about 5 h in a vacuum oven. The DSC analysis was carried out on a Perkin-Elmer DSC-7 with a heating and cooling rate 20°C/min. in the range of 50–250°C.

6. *Mechanical properties*

The specimen films prepared in 3 were cut into dumb-bell test pieces. The strength and elongation at break were measured on Instron 1122 at room temperature.

7. *Semipermeability of films*

Using CHCl_3 as the solvent, a 8 wt% solution of copolymer was prepared in a 20 ml round bottom flask and the excess solution was poured out after shaking by swirling. Add some distilled water into the flask after the solvent was evaporated to dryness at room temperature. A small balloon-like plastic bag could be peeled off from the flask-wall after water was poured out. The plastic bags obtained were used on the test of semipermeability of films.

RESULTS AND DISCUSSION

The hydrophobicity of Si-containing polyester-polyether copolymers was characterized by contact angle to water of the copolymer films. The results were listed in Table 2. It can be seen that the contact angles to water of the copolymer films increase obviously with increasing content of silicone incorporated, the more the content of silicone is, the larger the contact angle will be. It indicates that hydrophobicity of the copolymers is improved. It seems that hydrophobicity of the copolymers containing PBS is better than that of copolymers containing PBSO by comparing the data of II and IV or III and V in Table 2.

Table 2 Contact angles of the copolymer films to water

Copolymers	[I]	[II]	[III]	[IV]	[V]
Contact angles to water	60.7°	69.7°	75.0°	70.7°	82.7°

The XPS determination data further explained the above results. The ratio of silicon to carbon at different depth of copolymer films, which was expressed by the angle to the surface of the copolymers films, was shown in Table 3. It indicates that the ratio of silicon to carbon decrease with increasing the angle to the surface of the films (i.e. depth of the film). That means silicon was enriched at the surface of the Si-containing polyester-polyether copolymers. The migration of silicone to the surface of the copolymers contributes to the improvement of hydrophobicity of the copolymers.

Table 3 The ratio of Si/C at different angle to the air surface of films

Angle (°)	Ratio of Si/C in the copolymers			
	[II]	[III]	[IV]	[V]
5	0.8331	0.7816	0.5091	0.6762
35	0.3631	0.5835	0.3950	0.3938
60	0.2725	0.5816	0.3400	0.3033
85	0.2442	0.5246	0.2291	0.2980

Table 4 Gas permeability for O₂ and N₂ at 25°C

Copolymer	[I]	[II]	[IV]
J(O)[cc(STP)/cm ² ·sec·cm Hg]	2.86×10^{-7}	3.90×10^{-7}	4.64×10^{-7}
J(N)[cc(STP)/cm ² ·sec·cm Hg]	1.27×10^{-7}	3.22×10^{-7}	3.38×10^{-7}

The gas permeability data for O₂ and N₂ of the Si-containing polyester-polyether copolymers were listed in Table 4. It can be found that the permeability of O₂ and N₂ of polyester-polyether copolymers is greatly increased owing to introducing

organosilicone compounds into the copolymers.

The initial weight loss temperature (T_0) and half weight loss temperature ($T_{1/2}$), which were obtained from those curves measured on the heating weight loss balance, are listed in Table 5. It can be seen that the heat resistance of polyester-polyether copolymers is greatly improved due to the presence of organosilicone compounds. Moreover, it showed that the heat resistance of PBT-PBSO-PTMG is better than that of PBT-PBS-PTMG.

An interesting result was caught by the test on films, that the films made of Si-containing copolymer in hard segment were microporous membranes with semipermeability. It can be found that when adding a starch-KI solution into the plastic bags no liquid will ooze out through the plastic bag made of no-Si copolymer PBT-PTMG, but the plastic bags made of Si-containing copolymers are penetrable by the liquid. No blue colour appeared when introducing chlorine gas into the filtrate, but blue colour appeared at once after adding little starch into above solution owing to starch combining with I_2 produced from oxidizing KI by Cl_2 . It can be concluded that there is only KI, no starch in the filtrate, and the films made of Si-containing copolymers are semipermeable.

From DSC results shown in Table 6, it can be seen that the melting points (T_m) of the Si-containing copolymers drops markedly, indicating the formation of a random copolymer with hard segment (PBT-co-PBSO or PBT-co-PBS). ΔH_m of the Si-containing copolymers was decreased because of decreasing of both the rate of crystallization and the crystallinity.

Table 5 Weight loss temperature of the Si-containing copolymer

Copolymers	[I]	[II]	[IV]
T_0 (°C)	200	225	213
$T_{1/2}$ (°C)	388	404	395

Table 6 DSC results of the copolymers

Copolymers	[I]	[II]	[IV]
T_m (°C)	165.1	149.8	148.9
ΔH_m (J/g)	3.135	0.401	0.226

It is inevitable that the mechanical properties of the Si-containing copolymers (cf. Table 7) are worsened owing to the decreasing of crystallinity of the copolymers.

Table 7 Mechanical properties of the copolymers

Copolymers	[I]	[II]	[III]	[IV]	[V]
Tensile strength (kg/cm ²)	210	136	87	168	125
Elongation (%)	1400	1300	1400	1250	1400

Keywords:

Polyester-polyether copolymers; Organosilicon modification

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