

Investigation of Relationship between Surface Properties and Blood Compatibility of Blended Polyether Polyester Block Copolymer

Shen-guo WANG

Institute of Chemistry, Academia Sinica, Beijing, China

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ABSTRACT: The blood compatibility of polymer is strongly influenced by surface properties of multicomponent polyether polyester block copolymer, such as contact angle, water sorption and microphase separated structure of the copolymer. The X-ray photoelectron spectroscopy test shows that the concentration ratio of oxygen to carbon on the sample-air interface is greater than that in the bulk, suggesting the diffusion of ether-bond towards the air surface. The biggest contact angle, the greatest increasing degree of O/C, and the most tiny microphase separated structure were found in the polyether polyester block copolymer composed of 60%—(PTMGT) and 40%—(PEGT) as soft segment, and this was the best material for blood compatibility.

KEY WORDS Polyether / Polyester / Block Copolymer / Blend / Surface Property / Blood Compatibility /

It is well known that the microphase separated structure and suitable hydrophilicity/hydrophobicity of polymer are important factors for the polymer materials with excellent blood compatibility.¹⁻⁵ Polyether polyester block copolymer is one of the materials with excellent physicochemical properties developed from the 1970s.^{6,7} It can be blended with other polymer like silicone resin to form antithrombotic materials.⁸ We have also reported that the blood compatibility of polyether polyester block copolymer can be improved by grafting it with acrylamide.⁹ Later, we have reported the blood compatibility of mixed-polyether polyester block copolymer (MPEE) composed of two kinds of polyether, which possess different hydrophilicities, such as polyethylene glycol (PEG) and polytetramethylene glycol (PTMG) as soft segment component. By comparison of blood compatibility of MPEE with that of a blended polyether polyester block copolymer (BPEE) composed PTMGT-PET and PEGT-PET, it was found that almost all of MPEE

had better blood compatibility than that of BPEE. But an unusual phenomenon have been found in the BPEE (60/40), consisted 60% PTMGT-PET and 40% PEGT-PET. It displays the best blood compatibility as well as mechanical properties. It was considered to be attributed to the tiny microphase separated structure at that composition ratio.^{10,11} Until now there are however no report about the effect of composition on blood compatibility of polyether polyester block copolymer except the present paper.

EXPERIMENTAL

Synthesis, Purification and Determination of Polyether Polyester Block Copolymer

A mixture of dimethylterephthalate (DMT), ethylene glycol (EG), tetrabutyl titanate catalyst (Ti(OBu)₄) and polytetramethylene glycol (PTMG, mol. wt. 2200) or polyethylene glycol (PEG, mol. wt. 2000) undergoes an esterexchange reaction at 170—200°C and polycondensation reaction at 250°C/0.1 mmHg.

The polyether polyester block copolymers such as PTMGT-PET and PEGT-PET were obtained. The copolymer was purified by re-precipitation from chloroform solution into cold petroleum ether followed by the extraction with ethanol. The ratio of hard segment to soft segment of the purified product was determined by $^1\text{H NMR}$.¹¹

Preparation of Blended Polyether Polyester Block Copolymer

A mixture of purified PTMGT-PET and PEGT-PET was dissolved in chloroform with certain composition. After filtration, the solution was casted on a glass plate and evaporated the solvent at room temperature to prepare BPEE sample.

Blood Compatibility

1) Recalcification time test: Class test tube was coated with copolymer. Then platelet rich plasma (PRP) was added. After adding calcium chloride solution, the test tube was shaken, and starting time was recorded. The time at which the white precipitate appeared is measured to be the recalcification time.

2) Platelet sorption test: It was measured by improved Salzman Method¹² with disposable Platelet Sorption Test Tube using PRP, and was calculated by the eq 1

$$\text{Platelet sorption (\%)} = \frac{N_0 - N}{N_0} \times 100 \quad (1)$$

where N_0 is platelet number in the original PRP, and N is platelet number after the PRP was passed through the Platelet Sorption Test Tube.

X-Ray Photoelectron Spectroscopy (XPS)

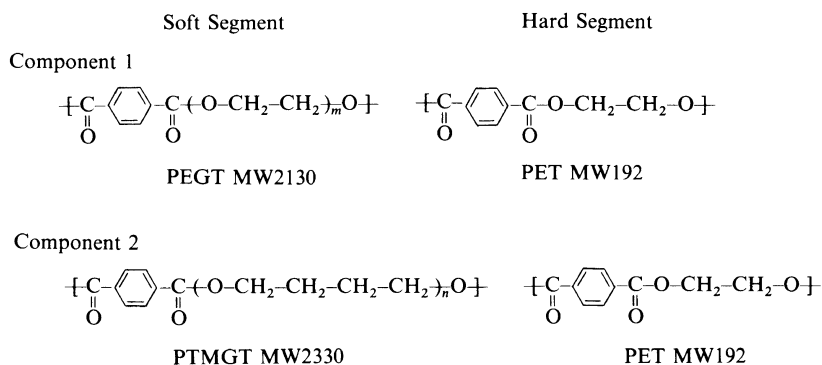
The XPS spectra were measured on KRATOS ES-300 with AL- K_{α} X-ray source at the pressure less than 5×10^{-8} mmHg. The energy scanning width was 25 eV and scanning speed was 0.1 eV s^{-1} . The sampling depth was controlled by changing the emission angle of electron beam.

Contact Angle Measurement

The contact angle of BPEE sample to water was measured on the air surface of the sample film by CA-D type Contact Angle Meter (Kyowa Kaimenkagaku Co., Ltd).

RESULTS AND DISCUSSION

A series of blended polyether polyester block copolymer (BPEE; Formula 1), which consists of various component ratio of PTMGT-PET to PEGT-PET was prepared. Both PTMGT-PET and PEGT-PET composed of same hard segment PET at 78.7 mol% and 21.3 mol% different hydrophilic soft segments, PTMGT and PEGT, respectively. It was found that the water sorption of BPEE increased with increasing PEGT content (Figure 1). It means



Formula 1. Blended polyether polyester block copolymer (BPEE).

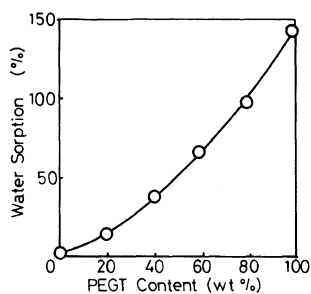


Figure 1. Dependence of water sorption on PEGT content.

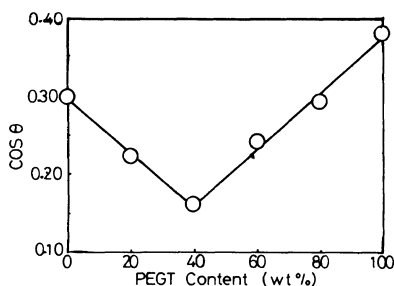


Figure 2. Dependence of contact angle on PEGT content.

that the hydrophilicity and hydrophobicity of the blend can be controlled by adjusting the ratio of these two components. Contact angle was used to characterize the surface free energy of a solid material, and the surface soakage of the material to water was estimated from it. The dependence of PEGT content of BPEE on the contact angle was shown in Figure 2. The biggest contact angle (*i.e.*, the smallest $\cos \theta$) was found for BPEE (60/40) sample composed of 60 mol% PTMGT-PET and 40 mol% PEGT-PET. However the surface of BPEE (60/40) was suggested to possess the weakest soakage to water, its water sorption was not the smallest. It was much higher than that of PTMGT-PET and about 1/3.5 of that of PEGT-PET. It can be suggested that each component has redistributed on the surface with shifting of component ratio. So that there is a conceptual difference between water sorption and surface hydrophilicity (or soakage) of material.

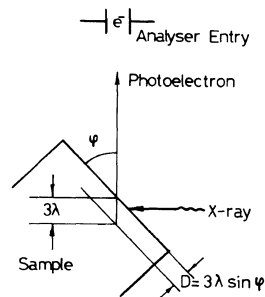


Figure 3. Relationship between sampling depth and emission angle.

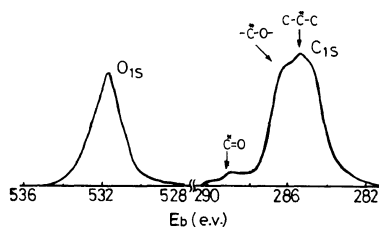


Figure 4. XPS spectra of O_{1s} and C_{1s} electrons of polyether polyester block copolymer.

The composition of sample surface has been evaluated by measuring the O/C ratio with XPS technique. Schematic relationship between sampling depth and emission angle was shown in Figure 3. The sampling depth D can be calculated by:

$$D = 3\lambda \cdot \sin \varphi$$

where D is the sampling depth; φ is emission angle; λ is average free path of electron, λ is about 50 \AA for ordinary polymers.^{13,14} In this work 20° of emission angle has been controlled, and sampling depth was 17 \AA . The XPS spectra of O_{1s} and C_{1s} electrons of BPEE were shown in Figure 4. It is observed that the O_{1s} XPS spectrum shows one peak with binding energy $E_b = 532.5 \text{ eV}$, and the C_{1s} XPS spectrum shows three peaks with binding energy $E_b = 280.5 \text{ eV}$ ($-\text{C}-\text{C}^*-\text{C}-$), $E_b = 286.4 \text{ eV}$ ($-\text{C}^*-\text{O}-$) and $E_b = 289.4 \text{ eV}$ ($\text{C}^*=\text{O}$). The relationship between spectrum peak area and element concentration¹⁴ is shown as eq 2

$$A = C\sigma\lambda\eta I \quad (2)$$

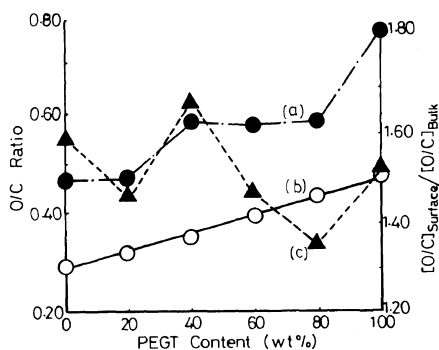


Figure 5. Dependence of composition on PEGT content: (a) O/C ratio at air-sample interface; (b) O/C ratio in the bulk average; (c) $[O/C]_{\text{Surface}}/[O/C]_{\text{Bulk}}$.

Where C is the element concentration; σ is the crosssection of photoelectron; η is equipment coefficient for electron determining; I is the X-ray intensity; and A is the spectrum peak area. The ratio of oxygen to carbon (O/C) can be calculated according to eq 3.

$$O/C = KA_{O_{1s}}/A_{C_{1s}} \quad (3)$$

where K is a constant. The ratios of O/C on the air-sample interface (determined by XPS) and in the bulk (determined by ^1H NMR) were shown in Figure 5(a) and (b), respectively. It is clear that the O/C on the interface is greater than that in the bulk. This suggests that the ether bond has diffused towards the air surface, and more soft segment has been found on the interface than in the bulk. This concentration gradient was attributed to the diffusion of PTMG towards the air surface due to its lower surface free energy than PEG.^{2,15} By comparing the ratios of $[O/C]_{\text{surface}}/[O/C]_{\text{bulk}}$, it has been found that the greatest increase of the O/C ratio occurred for the BPEE (60/40) sample (Figure 5(c)). It means that the most of PTMG has existed at the BPEE (60/40) surface than the other part. There is the weakest soakage for BPEE (60/40) surface, because the hydrophilicity of PTMG is much lower than that of PEG. This may be reason why the biggest contact angle is seen for the BPEE (60/40). The best blood compati-

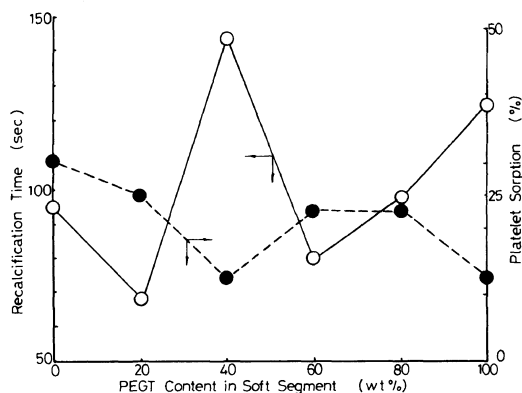


Figure 6. Dependence of blood compatibility on composition of BPEE.

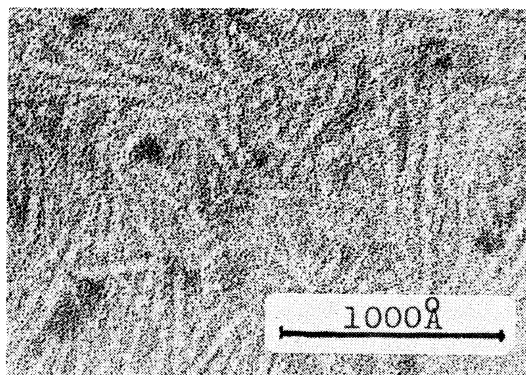


Figure 7. TEM photograph of BPEE (60/40).

bility, such as the longest recalcification time and the smallest platelet sorption also existed for the sample of BPEE (60/40) as seen in Figure 6.

It has been reported that all kinds of polyether polyester block copolymers possess microphase separated structure.¹¹ We found more tiny microphase separated structure (about 50Å) in the BPEE (60/40) as shown in Figure 7. The smaller dimension of microdomain, suggesting the best miscibility, was found for the samples having the ratio of PTMGT-PET to PEGT-PET in 60% to 40%.

As mentioned above, the blood compatibility of PEGT-PET is better than that of PTMGT-PET (see Table I). It is attributed to

Table I. Dependence of properties on composition of copolymer

PTMGT	Water sorption	Contact angle	O/C atom ratio at surface	Recalcification time	Platelet sorption	Tensile strength	Elongation at break
PEGT	%	$\cos \theta$		s	%	kg cm^{-2}	%
100/0	0.8	0.30	0.46	95	30.0	1.84	900
60/40	40	0.16	0.58	144	12.5	1.60	915
0/100	140	0.40	0.71	125	12.5	1.31	554

the PEGT soft segment, which is the same effect as observed on polyurethane.¹⁶ However, the biggest contact angle, the greatest increase of the O/C ratio, and the more tiny microphase separated structure were found for BPEE (60/40). Furthermore, the best blood compatibility and the best mechanical properties were also observed in the sample with that component ratio. Therefore it is concluded that the blood compatibility of BPEE is affected strongly by the surface composition, the surface free energy of each component and the state of microphase separation.

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