

ESCA STUDIES ON SURFACE COMPOSITION OF SEGMENTED POLYURETHANE*

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ABSTRACT

Segmented polyurethanes (SPU) have been used as an important biomedical material, of which the hemocompatibility is determined mainly by the surface properties of the polymer. ESCA has been used in the present study to characterize the surface composition of SPU samples with different degree of phase segregation. Our experimental results show that (1) the ratio of O/N on polymer-air interface is greater than that in the bulk, i.e., more soft segment is found on the surface than in the bulk average; (2) the soft segment is more abundant on the surface for the sample with better phase segregation; (3) within about 50Å thickness of the air facing side the composition variation of the sample with better phase segregation is greater than the sample with poor phase segregation.

INTRODUCTION

Segmented polyurethanes (SPU) have been considered for use as an important biomedical material because of their excellent mechanical properties, chemical stability and good hemocompatibility. It is widely recognized that the hemocompatibility of SPU is determined mainly by its surface composition. The composition of some SPU used as biomedical material was investigated by using Fourier transform IR internal reflection spectroscopy^[1] and electron spectroscopy for chemical analysis (ESCA)^[2, 3]. These results^[1-3] showed that more soft segment is found on the surface than it would be expected from the bulk average. Previous studies^[1-3] indicated that the chemical composition and processing variables affected the surface properties of SPU, but the relation between the bulk structure and surface properties have received relatively little attention. Therefore ESCA has been used to characterize the surface chemical composition of two SPU samples with different chain structure and to relate the surface composition to bulk property and microphase segregation.

EXPERIMENTAL

Materials

Samples of SPU were synthesized from 4, 4'-diphenylmethane diisocyanate (MDI), polytetramethylene oxide (PTMO) and with ethylene diamine (ED) or 1, 4-butadiol (BD) as chain extender. Samples extended with ED and BD are designated as group A and group B respectively. Group A samples have the mole ratio of 3 : 2 : 1 for MDI : ED : PTMO (M.W. 1800), while group B samples have the mole ratio 2 : 1 : 1 for MDI : BD : PTMO.

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(M. w. 1000). SPU samples using for ESCA measurement were obtained from 5% DMF solution by casting it on clean aluminum plate and dried in an oven at 60°C for more than 24 hr.

Model compounds

In order to assign the ESCA peaks and to obtain the total correction factor for quantitative analysis, hard segment and soft segment prepolymer were used as model compounds. The hard segment prepolymer was prepared by reaction of MDI with ED or BD, the soft segment prepolymer is polytetramethylene oxide (M. w. 1800).

ESCA measurement

ESCA spectra were obtained on a ES-300 electron spectrometer by using Mg $K\alpha$ radiation at 10^{-8} torr vacuum and at ambient temperature. The window was set at 12.5 eV. The scan rate of 0.02 eV/sec was used for all the runs. The half-width of $Ag_{3d\frac{5}{2}}$ ESCA peak is 0.9 eV.

For the depth profile of compositional variation within the outermost few tens Å of the polymer-air interface, the angular dependent ESCA (ESCA (θ)) technique has been used in this study. ESCA spectra were measured at take-off angle $\theta = 30^\circ$ and 80° . Fig. 1 is a schematic diagram of take-off angle. The relation between take-off angle and effective sampling depth is expressed as

$$Ae' = Ae \sin \theta \quad (1)$$

where Ae is the sampling depth at take-off angle $= 90^\circ$ and Ae' at take-off angle $= \theta$.

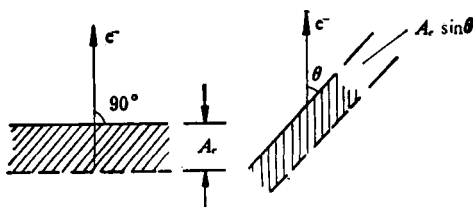


Fig. 1 Scheme of take-off angle

The sampling depth can be calculated from average free path of electron in polymer⁽⁴⁾, for example, Ae' is 50 Å at $\theta = 80^\circ$. By the same equation Ae' is 25 Å at $\theta = 30^\circ$.

RESULTS AND DISCUSSION

1. Assignment of ESCA peaks of SPU

The ESCA spectra of the air facing surface of group A sample are shown in Fig. 2. There are three C_{1s} ESCA peaks for carbon core electron. The major C_{1s} peak has binding energy B. E. of 285.0 eV and two small peaks have B. E. of 286.5 and 288.7 eV, respectively. The oxygen and nitrogen have single ESCA peak with binding energy of 532.7 and 400.0 eV respectively, are shown in Fig. 2 as well.

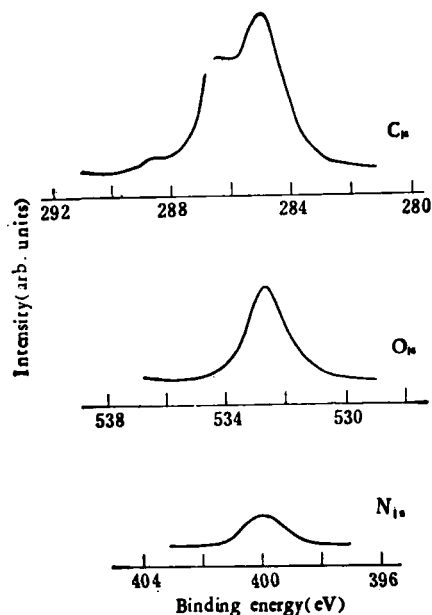


Fig. 2 ESCA spectra of group A sample

The ESCA spectra of group B sample are similar to those of group A sample.

In order to assign ESCA peaks of SPU samples, ESCA spectra of model compounds were measured and shown in Fig. 3 and 4.

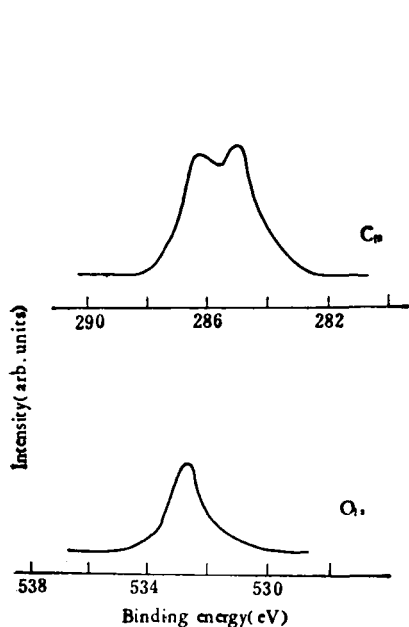


Fig. 3 ESCA spectra of pure PTMO model compound

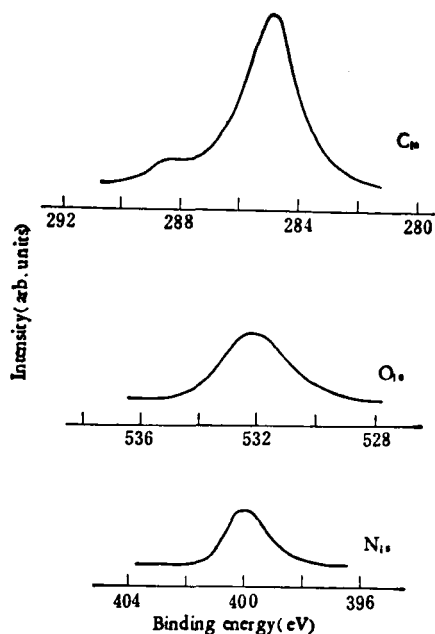


Fig. 4 ESCA spectra of the hard segment model compound (MDI:ED) of group A

The ESCA spectra of PTMO are shown in Fig. 3, in which two C_{1s} peaks of almost equal intensity are observed. Because the chemical structure of PTMO is $\text{-(O-CH}_2\text{-CH}_2\text{-CH}_2\text{-)}$, carbons are in two different chemical environment, i. e., $\text{-(CH}_2\text{-CH}_2\text{-)}$ and $\text{-(O-CH}_2\text{-)}$. The former C_{1s} B. E. is 285.0 eV, being similar to polyethylene while the later C_{1s} B. E. is 286.5 eV ^[2]. A single O_{1s} peak appears at 532.7 eV since oxygen in PTMO is in an identical environment.

Fig. 4 shows the ESCA spectra of hard segment model compound of group A sample.

The chemical structure of the polymer is $\text{-(HN-CO-NH-}\langle\text{C}_6\text{H}_4\text{)-CH}_2\text{-}\langle\text{C}_6\text{H}_4\text{-NH-CO-NH-CH}_2\text{-CH}_2\text{-)}$, carbons are in two different environment. The major C_{1s} peak at 285.0 eV include both aliphatic carbon and aromatic carbon since these two carbons are approximately same chemical shift. A small C_{1s} peak at 288.5 eV is due to the contribution of carbonyl carbon. The O_{1s} peak at 531.9 eV is due to carbonyl oxygen. The N_{1s} peak at 399.7 eV is due to urea carbonyl nitrogen.

ESCA spectra of group B are similar to those of group A, but the ESCA peaks were shifted slightly since -O-CO-NH- sequence is in place of -HN-CO-NH- sequence in sample A. Certain chemical shifts appeared, i. e., C_{1s} B. E. is 285.0 eV and 289.7 eV, O_{1s} is 532.1 eV and N_{1s} is 400.2 eV.

By comparing ESCA peaks of model compounds with those of SPU samples, all ESCA peaks of samples were assigned, as shown in Table 1.

Table 1 ESCA peak position and assignment of SPU

ESCA peak	Peak position (eV)	Assignment
C_{1s}	285.0	$\text{--CH}_2\text{--}$
	286.5	--C--O--C--
	288.7	$\begin{array}{c} \text{O} \\ \parallel \\ \text{--HN--C--NH--} \end{array}$
	289.4	$\begin{array}{c} \text{O} \\ \parallel \\ \text{--O--C--NH--} \end{array}$
O_{1s}	532.7	$\text{--C--O--C, --HN--C--NH, --O--C--NH--}$ $\begin{array}{ccc} \parallel & & \parallel \\ \text{O} & & \text{O} \end{array}$
N_{1s}	400.0	$\begin{array}{c} \text{--HN--C--NH--} \\ \parallel \\ \text{O} \end{array}$
	400.1	$\begin{array}{c} \text{--O--C--NH--} \\ \parallel \\ \text{O} \end{array}$

2. Quantitative measurement of soft segment to hard segment ratio of SPU samples

Since the nitrogen is originated only from hard segment and the oxygen is mostly originated from soft segment, so that, the ratio of O_{1s}/N_{1s} ESCA peak is used to characterize the

relative content of soft/hard segment^[5]. The relationship of atom ratio O_{1s}/N_{1s} and area ratio A_O/A_N of ESCA peak is given by

$$O_{1s}/N_{1s} = (A_O/A_N) (C_N/C_O) (\sigma_N/\sigma_O) \quad (2)$$

where A is the area of ESCA peak, C is the kinetic energy correction factor, σ is the cross section per atom for photoionization of the particular level, and subscript O and N represent oxygen and nitrogen. According to references [6] and [7], $C_N/C_O = 0.984$ and $\sigma_N/\sigma_O = 0.621$ were calculated. Thus equation (2) can be written as

$$O_{1s}/N_{1s} = K \times A_O/A_N = 0.611 \times A_O/A_N \quad (3)$$

where $K = 0.611$ is called total correction factor. So, it is convenient for quantitative measurement of the O_{1s}/N_{1s} from ESCA peak area ratio A_O/A_N .

The O/N ratio of compounds obtained from ESCA and chemical analysis are shown in Table 2, from which a good agreement between the results of two methods is observed.

Table 2 O/N ratio of model compounds

Model compound	O/N		O/C	
	ESCA	Chem. analysis	ESCA	Calculated
PTMO (M. w. 1800)	—	—	0.24	0.25
Hard segment (A)	0.57	0.71		
Hard segment (B)	2.7	2.2		

The O_{1s}/N_{1s} ratio of group A and B samples at different take-off angle are shown in Table 3.

Table 3 Surface composition and bulk property of SPU sample

Sample	O_{1s}/N_{1s}		$\Delta(O_{1s}/N_{1s})/\Delta\theta$	Bulk properties		
	$\theta = 80^\circ$	$\theta = 30^\circ$		O/N*	T_g ($^\circ\text{C}$)	ΔE (Kcal/mole)
A ₁	5.5	7.1	0.032	4.5	-54	30
A ₂	5.2	8.5	0.066	4.4	-56	—
B ₁	7.6	10.8	0.064	4.7	-28	66
B ₂	8.5	13.5	0.100	5.0	-36	35

* Chemical analysis

3. Relation between the surface composition and bulk property

From the view of microphase segregation of SPU we consider that the ratio of soft/hard segment on the surface should relate to its bulk microphase segregation. The experimental

results listed in Table 3 demonstrate this idea. From Table 3 the following conclusion can be drawn.

(1) The ratio of O_{1s}/N_{1s} on surface of the sample is greater than that in bulk for all samples, i. e., more soft segment is found on the surface than that would be expected from the bulk average. Moreover, the angular dependent ESCA results (refer to $\Delta(O_{1s}/N_{1s})/\Delta\theta$ in Table 3) show that O_{1s}/N_{1s} at $\theta = 30^\circ$ is greater than O_{1s}/N_{1s} at $\theta = 80^\circ$. It is interpreted as the low surface energy characteristic of the component which is more abundant on the polymer-air interface^[8]. Certainly, in the present system soft segment polyether has lower surface energy comparing with the hard segment.

The surface composition on air facing and substrate sides were measured. Results show that the soft segment was abundant on both surfaces, but it was more abundant on the air surface, as shown in Table 4.

Table 4 Surface composition on air and substrate surface

Sample	O _{1s} /N _{1s}				O/N Chem. anal.
	SPU-air interface		SPU-substrate interface		
	$\theta=80^\circ$	$\theta=30^\circ$	$\theta=80^\circ$	$\theta=30^\circ$	
Group A	4.3	9.2	4.0	6.6	3.7
Group B	6.6	8.9	6.2	6.6	5.6

(2) An interesting comparison can be made between the O_{1s}/N_{1s} results of sample A_1 and A_2 , as well as B_1 and B_2 in Table 3. As we have mentioned above, each group of samples has the same bulk chemical composition and molecular weight of soft segment, but their surface composition differs apparently from each other. According to transmission electron microscopy and dynamic mechanical analysis results^[9], the group A and B samples show two phase structures, but two samples of each group have different degree of phase segregation. The degree of phase segregation can be estimated by the T_g and active energy ΔE of glass transition of the soft segment phase. The sample with better phase segregation has low T_g and ΔE . So that, the T_g and ΔE of soft segment phase can be used to characterize the phase segregation of SPU^[10].

Table 3 shows that samples with better phase segregation (A_2 , B_2) have more soft segment on surface than samples with poor phase segregation (A_1 , B_1).

(3) Angular dependent ESCA results (refer to $\Delta(O_{1s}/N_{1s})/\Delta\theta$ in Table 3) show that the compositional variation of samples with better phase segregation is greater than samples with poor phase segregation.

Furthermore, our results show that there is a reasonable correlation between bulk structure and composition of SPU.

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