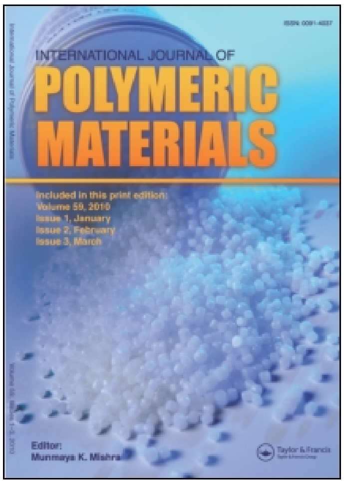

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Kinetic Aspects of Hydrolytic Resistance of Avtocan and Biomer Segmented Polyurethanes

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Degradation of film samples, representing of segmented polyesterurethanes (Avcotan and Biomer) in water and acidic solutions (acidic phosphastes) was investigated. We found, that Avcotan, representing copolymers of segmented polyurethanes with polydimethylsiloxane, degradated in water with noticeable rate, whereas Biomer samples were found hydrolytically stable. It was shown, that degradation from Avcotan sample surface was stipulated by decompostiion of siloxane component as a result of hydrolysis. The values of decomposition rate constant, allow us to predict the duration of degradation for surface layers of polyesterurethanes (Avcotan), responsible for thromboresistance.

Keywords: Segmented polyesterurethanes; biomedical applications; hydrolytic degradation

INTRODUCTION

Thromboresistant materials, based on segmented polyesterurethanes (PEU) are widely used in medical applications. Their characteristic feature is inhomogeneity of morphological structure of surface layer resulting from different ratios of flexible and rigid segments [1, 2].

The application of these materials involves their implantation into vital organism medium, which possesses active components, such as

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water, salts, enzymes, as well as preliminary steam treatment, required for sterilization.

In this connection it was desirable to establish the resistance of PEU to water and water solutions of salts. For this purpose we have investigated the process of segmented polyesterurethanes degradation – Avcotan-51 (Avco-Everet Company) and Biomer (Eticon Company) – in water and phosphate buffer pH = 7.4.

RESULTS AND DISCUSSION

Avcotan-51 films were obtained from 6% polymer solution in tetrahydrofurane and dioxane (2 : 1) in argon atmosphere at 12 – 14% humidity in dust free vessel; Biomer films were obtained from 10% solution in dimethylacetamide at 50°C.

Films of various thickness (300 – 500 μm) were obtained by repeated dipping of glass plates into the solution. The degradation of samples was performed in a special glass radiation vessels at 37, 58, 80 100°C in water and in phosphate buffer having pH = 7.4. After equal time periods, the samples were washed carefully in distilled water and dried in vacuum at 80°C to constant weight. Degradation kinetics was studied by means of spectrometry method on Pye Unicam SP8-100 and by gravimetry method recording the mass losses. Tensile strength of polymer films was determined on Instron. Kinetics of water sorption into polymers was determined by Mac-Bain balance with quartz spiral, having the sensitivity of 0.5 mg/mm.

Avcotan-51 by its structure, consisted is a complex segmental polyesterurethane and polydimethylsiloxane (PDMS) block-copolymer, with the segments dispersed in basic polymer matrix. In general case, the hydrolytic decomposition of these polymers may proceed independently. Therefore, it was interesting to investigate hydrolytic degradation of PDMS and PEU separately. For this purpose we prepared PDMS films, vulcanizing liquid polymer at room temperature in presence of the catalyst (1% of tetraethoxysilane and tin-octoate). Then we studied their degradation in water and phosphate water solutions. Kinetic curves of mass losses are shown in Figure 1.

As it is seen from Figure 1, the mass losses of PDMS samples proceed according to zero order by polymer. Sample stability practically

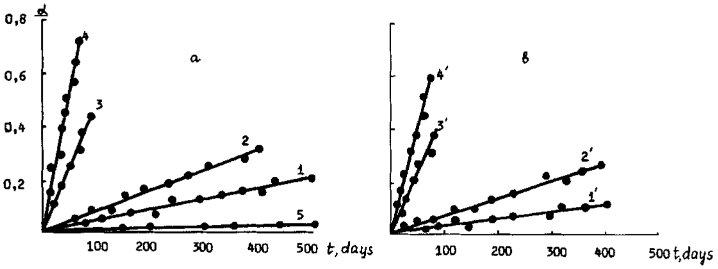

FIGURE 1 Kinetic curves of PDMS samples mass losses in water (a) and phosphate buffer pH 7.4 (b) at temperatures: 37 – (1, 1'), 58 – (2, 2'), 80 – (3, 3') and 100°C – (4, 4'), air, 37°C – (5).

did not change during the degradation process. The data obtained can be explained, assuming that decomposition proceeds from the sample surface. This assumption is supported by extremely low water solubility in PDMS, which we could not experimentally determine. Apparently, it is less than 0.05%. The weight change due to decomposition proceeding from sample surface (S-type), is described by the following equation:

$$m = m_o - K^S_{\text{eff}} tS \tag{1}$$

where m and m_o – initial and present sample weight, respectively: K^S_{eff} – efficient rate constant of polymer decomposition from the surface; S – surface.

Polymer decomposition by volume (V-type) under the influence of solved water does is negligible, which is corroborated by, the absence of polymer resistance losses. Similar results were obtained for phosphate buffer. Table I shows the values of effective rate constants and activation energies.

TABLE I Efficient rate constants of PDMS degradation ($S_o = 6\,\text{cm}^2, m_6 = 0.5\,\text{g}$) in water and phosphate buffer at various temperatures

T, °*C*	*k*, *g cm*$^{-2}$ *days*$^{-1}$	
	Water, *pH* 6.5	*Phosphate buffer*, *pH* 7.4
37	2.0×10^{-5}	1.8×10^{-5}
58	7.5×10^{-5}	7.3×10^{-5}
80	4.0×10^{-4}	3.8×10^{-4}
100	1.0×10^{-3}	0.9×10^{-3}

On the basis of experimental data, we can express the mass loss as follows:

$$m = m_o - 10^5 e^{-14000/RT} tS, \tag{2}$$

where m is measured in gramms, S – in cm^2, t – in days.

Correlation of rate constant values shows, that active agent, causing PDMS degradation, is water, because acceleration of decomposition process is not observed in presence of phosphate ions.

To study hydrolytic resistance of PEU we investigated Biomer film degradation in water and phosphate buffer. We found, that neither mass change nor degradation product accumulation of product was absorbing in UV-range of spectrum, during 100 days at 100°C in water and phosphate buffer, took place. It is possible that the decomposition proceeds by volume. However, we obtained no changes of stability and specific viscosity of the samples, treated by degradation in water during a long time.

Thus, it may be concluded, that PDMS component of Avcotan-51 is moderately hydrolytically stable, whereas polyesterurethane component is hydrolytically stable, in practice, as well as, under experimental conditions.

According to ESCA data [4, 5] and MNPVO in infrared range [6], different content of PDMS is observed in surface layers, facing the air and glass support With Avcotan-51 PDMS concentration is significantly different on the surface and in the volume. In this connection it is interesting to investigate the proceeding of degradation process of Avcotan-51.

Figure 2 shows kinetic curves of polymer mass decrease in water at various temperatures. Kinetic curves possess two characteristic parts: abrupt mass decrease (0.5 – 1% of film mass) occurs at the initial part which is followed by a linear part, relating to a slower and stationary degradation process.

To clarify the type of Avcotan-51 decomposition it is required to obtain the data of water sorption. We have studied kinetics of water sorption in Avcotan-51 and Biomer in various conditions. Diffusion coefficient was calculated according to the following equation:

$$M_t = M_\infty\left(1 - \frac{8}{\pi^2}\cdot e^{-\pi^2 Dt/l^2}\right), \tag{3}$$

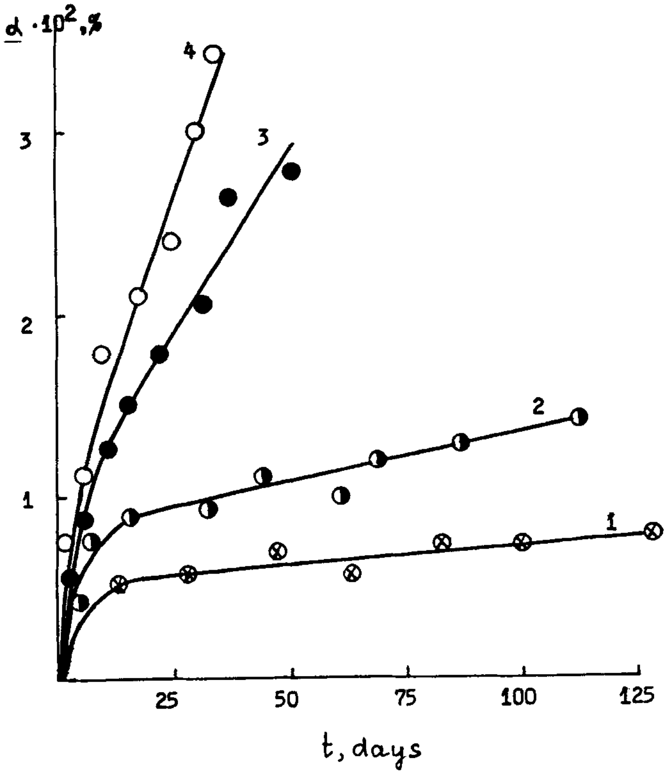

FIGURE 2 Kinetic curves of Avcotan-1 films mass decrease in water at various temperatures; 37 – (1), 58 – (2), 80 – (3) and 100°C – (4).

where M_t and M_∞ – water amounts, sorbed by the film of l thickness at time moment t and in sorptional equilibrium state, respectively.

Table II shows limit sorption values and coefficients of water diffusion in Avcotan-51 and Biomer. These parameters were found similar for both polymers. Considering, that water is practically insoluble in PDMS, we can assume, that water, sorbed by Avcotan-51 will be localized in polyesterurethane component of this material.

The following explanation of macrokinetics of Avcotan-51 degradation can be suggested, based on the presented data.

The first part of kinetic curve related to PDMS degradation in Avcotan-51 surface layer. Degradation rate decreases with time, that relates to the decrease of PDMS concentration in the surface layer and

TABLE II Limit sorption values, sorbtion heat, coefficients of water diffusion and activation energies in Biomer and Avcotan-51

$T, °C$	$C \times 10^2 g/g$	$\Delta H, Kcal/mol$	$D \times 10^6, cm^2/s$	$E, Kcal/mol$
BIOMER				
37	1.0		0.7	
50	1.6	8 ± 1	1.3	9 ± 1
60	2.5		2.2	
AVCOTAN-51				
37	1.2		0.4	
50	1.8	8 ± 1	0.9	10 ± 1
60	2.9		1.5	

the decrease of surface water concentration. The initial rate of the process is close to corresponding rate of PDMS film degradation of the same area.

The second part of kinetic curve relates to PDMS degradation in domains, distributed uniformly in deeper layers of Avcotan-51. PDMS degradation proceeds on domain surface under the influence of water, solved in the polymer. As total domain surface is known, we show (Tab. I) the rates of degradation process at various temperatures. It is interesting to point out, that activation energy of degradation, calculated from these rates for PDMS films, is close to the value of activation energies for Avcotan-51 and Biomer (Tab. II).

Consequently PDMS component is extracted from Avcotan-51 at this stage of degradation process, which must influence mechanical properties of the polymer. Actually, the tensile strength and calculated resistance of Avcotan-51 films decreases during degradation proceeding. Similar data were obtained for Avcotan-51 degradation in phosphate buffer, indicating that water played the role of active agent as in case of PDMS films. Phosphate ions do not cause any catalytic influence.

Thus it can be concluded, that Biomer possesses high hydrolytic resistance in water and water solutions of salts. Avcotan-51, however, possesses lower hydrolytic resistance, due to PDMS hydrolysis.

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