PHOTOOXIDATION OF SILOXANE POLYMERS UNDER VACUUM ULTRAVIOLET IRRADIATION.

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Vacuum ultraviolet(VUV) irradiation (wavelength 147 nm) of siloxane polymers in the presence of air was studied using ATR FTIR and XPS spectroscopy. The ATR FTIR study revealed the formation of CO and OH groups in the surface layer depending on irradiation time and air pressure. The concentrations of CO and OH groups level off with the increase of irradiation time and pass through the maximum value with the increase of pressure in the range of 0.1-100 torr. The XPS study of irradiated polysiloxane films demonstrated that intermolecular crosslinking via oxygen atoms also takes place on the polymer surface. The concentrations of the most important oxygen species O and O₃, produced by VUV photolysis of air and coming to the polymer surface were calculated for the air pressure range 0.1-100torr. The photooxidation mechanism for siloxane polymers under VUV irradiation in air has been proposed.

1. Introduction

Interest in using siloxane polymers has been steadily increasing because of their good biocompatibility, high gas permeability, unique optical and mechanical properties [1,2]. A study of VUV irradiation of siloxane polymers is of great interest for understanding the mechanism of photooxidation and possible application of this process for surface modification purposes. In this work we have investigated the kinetics and mechanism of chemical changes occurring in the surface layer of siloxane polymers under the action of resonant vacuum ultraviolet irradiation with the wavelength 147nm in the presence of air.

2. Experimental methods.

Samples of siloxane polymers (diameter 10mm, thickness 1-3mm) were irradiated in vacuum chamber at air pressure 0.1 - 100 torr, flow rate 20 cm³(STP)/min and room temperature. The hollow cathode gas discharge resonant Xe lamp KsR-2A [3] equipped with MgF₂ window and located at a distance 30mm from

the polymer surface has been used. The radiation intensity was measured by "sun blind" vacuum photodiode.

IR spectra of polymer surface layer were recorded on Perkin-Elmer model 1720X FTIR spectrometer using attenuated total reflection technique (Harrick ATR attachment, KRS-5 prism, angle 45° , 25 reflections).

The treated polymer surfaces were also analyzed by X-ray photoelectron spectroscopy on Kratos model XSAM 800 spectrometer employing MgK_α exciting radiation. The spectra of C_{1s} , O_{1s} and Si_{2p} regions were registered.

The structures of two investigated siloxane polymers are shown below:

3. Results and discussion.

Fig. 1 shows ATR FTIR spectra of polymer I before (curve 1) and after (curve 2) VUV treatment as well as the difference spectrum (curve 3). Two new bands observed in the regions $3000\text{--}3400\text{cm}^{-1}$ and $1700\text{--}1740\text{cm}^{-1}$ in the difference spectrum can be attributed to OH and CO stretching vibration respectively.

Fig.1 IR (ATR) spectra of the polymer I:1 - untreated,
2 - VUV treated ($t=30$ min, $p=3$ torr),
3 - difference spectrum.

Table 1 summarizes the results of XPS surface study of polymer 1 before and

after irradiation.

Table 1. Summary of changes in elemental composition due to VUV treatment of polymer I. 1-untreated sample, 2-VUV treated sample (t=20 min, p=2.5torr, l=3cm)

N smp.	Si2p			C1s	O1s	
	(CH ₃) ₂ -Si- -(-O) ₂	(CH ₃)-Si- -(-O) ₃	Si-(-O) ₄	-	-	
	Binding energies.					
	103.5	103.2	104.0	285	532.5	
	Atoms concentrations, %					
1	21	-	-	58	21	-
2	14	2.9	2.3	52.8	28	39

The C_{1s} (285.0eV), O_{1s} (532.5eV) and Si_{2p} (103.5eV) XPS peaks were investigated. Three components were used for simulation of Si_{2p} peak. The first one is due to Si atoms in $\text{Si}(\text{O}_2)$ environment (103.5eV), the second one is attributed to Si atoms bonded to three oxygen atoms $\text{Si}(\text{O}_3)$ (103.2eV) and the third one is due to Si atoms bonded to four oxygen atoms $\text{Si}(\text{O}_4)$ (104.0eV). The presence of this three components in siloxane polymers exposed to oxygen plasma afterglow was observed and identified earlier [2] by using appropriate model compounds. Analysis of possible structures of treated polymers based on C, O, and Si atomic concentrations obtained from XPS spectra shows that $\text{Si}(\text{O}_3)$ and $\text{Si}(\text{O}_4)$ structures could be attributed to the intermolecular crosslinks formed via oxygen atoms. Therefore as indicated in Table 1 about 39% of Si atoms have been involved in intermolecular crosslinks by VUV irradiation. Comparing in wide shape of C_{1s} spectra of irradiated polymer with that of untreated sample also

suggests the formation of CO and COH groups under irradiation. Very similar changes in structure appeared in the formation of CO, OH groups and intermolecular crosslinks were observed for polymer II after irradiation.

It is evident that changes in structure caused by the simultaneous action of incident VUV radiation and active oxygen species O, O₃, O₂(¹Δ_g) etc. produced by VUV photolysis of air and come to the polymer surface. The gaseous products eliminated from polydimethylsiloxane under VUV 147nm irradiation were studied earlier [4] by massspectrometric method. It has been shown that H₂, CH₄, and C₂H₆ were the main products of PDMS photolysis in vacuum. Initial quantum yields were found to be 1.2*10⁻², 6.4*10⁻² and 1.0*10⁻² for H₂, CH₄ and C₂H₆ respectively. Analysis of experimental data led the authors to the conclusion that removal of H and CH₃ radicals was the main primary processes induced by VUV irradiation. Based on these conclusions and on the values of quantum yields obtained for stable gaseous products the quantum yields of polymer macroradicals -Si(CH₃)₂-O-Si(CH₃)- (1) and Si(CH₃)₂-O-Si(CH₃)(CH₂)- (2) formed as a result of CH₃ and H abstraction were calculated to be 8.2*10⁻² and 8.8*10⁻² respectively.

Among active oxygen particles, formed as a result of VUV absorption in air the O and O₃ species play the most important role in surface photooxidation processes. Actually these particles have the maximum rate constants in the reactions with surface stable groups and with macroradicals produced under VUV irradiation. The processes of formation and destruction of O and O₃ active species can be describe by the following set of basic reactions:

where reactions 1-6 describe O and O₃ formation and destruction homogeneous processes occurred during VUV (147nm) photolysis of air [5] whereas reactions 7-13 represent heterogeneous processes going on at the surface and on the VUV lamp window. The needed probabilities of heterogeneous processes for O and O₃ particles were taken from [6,7]. Based on reactions kinetic described above and one-dimensional diffusion model the following differential equations for O and O₃ concentrations can be written:

$$\frac{\partial [O]}{\partial t} = D_1 \frac{\partial^2 [O]}{\partial x^2} + \varphi_1 I(x) [O_2] - k_{1,2} [O] [O_2, N_2]^2 - k_3 [O] [O_3]$$

$$\frac{\partial [O_3]}{\partial t} = D_2 \frac{\partial^2 [O_3]}{\partial x^2} + k_{1,2} [O] [O_2, N_2]^2 - k_3 [O] [O_3]$$

with boundary conditions:

$$D_1 \frac{\partial [O]}{\partial x} \Big|_{x=0} = 1/4 [O] \Big|_{x=0} \cdot V_O \cdot \gamma_6 \quad D_2 \frac{\partial [O_3]}{\partial x} \Big|_{x=0} = 0$$

$$D_1 \frac{\partial [O]}{\partial x} \Big|_{x=l} = 1/4 [O] \Big|_{x=l} \cdot V_O \cdot \gamma_6 \quad D_2 \frac{\partial [O_3]}{\partial x} \Big|_{x=l} = 1/4 [O_3] \Big|_{x=l} \cdot V_{O_3} \cdot \gamma_3$$

where p - is the O₂ partial pressure; x - is the distance from VUV lamp; D₁, D₂ - are the diffusion coefficients for O and O₃ respectively; I(x) = I₀ * exp[-k(p)*x] - the intensity of VUV lamp at the distance x; k(p) - the O₂ absorption coefficient for 147nm radiation.

The main results of computer calculation of atomic oxygen concentration at the polymer surface as a function of air pressure and the distance between polymer sample and VUV lamp are shown in Fig. 2,3.

Fig.2 Concentrations of O atoms at the polymer surface as a function of oxygen pressure for the different distances from VUV lamp.

The concentration of atomic oxygen at the vicinity of polymer surface reaches a maximum value and fall off with further increase of pressure. It should be

noted that higher maximum concentrations of O are reached at higher distances but at lower O₂ partial pressure. Ozon concentrations vs O₂ pressure follow trends very similar to that obtained for atomic oxygen concentrations. However for our pressure range the value of ozone concentration was found to be 3-4 orders of magnitude lower than that of atomic oxygen. Therefore O₃ molecules appear to play unimportant role in the photooxidation process under our experimental conditions. The intensity of VUV radiation according to Lambert-Bear's law decreases exponentially with the increase of distance and O₂ partial pressure. One can thus expect that the rate of photooxidation under the simultaneous action of VUV radiation and oxygen atoms will exhibit an extreme dependence on the air pressure. This conclusion was found to be corroborated by experimental data. As illustrated in Fig. 4-7, the concentrations of the main products of photooxidation CO and OH groups level off at the irradiation times more than 30 min and take the maximum value at the same pressure 2.5 torr for the irradiation distance 3cm.

The mechanism of VUV photooxidation process leading to the formation of CO and OH groups as well as intermolecular crosslinks can be represented by the following basic reactions:

Fig.3 Concentrations of O atoms at the polymer surface as a function of distance from VUV lamp for the different oxygen pressures(10, 20, 40, 60, 80,100 torr).

Fig.4 Evolution of OH groups at the surface of polymer I with VUV irradiation time.

Fig.5 Evolution of CO groups at the surface of polymer I with VUV irradiation time.

Fig.6 Effect of air pressure on the concentration of OH groups produced by VUV irradiation.

Fig.7 Effect of air pressure on the concentration of CO groups produced by VUV irradiation.

There are three groups of reactions shown above. The first one includes the reactions of radicals formation under the action of VUV radiation and oxygen atoms. The second one describes the reactions of radicals with O_2 leading to the formation of peroxide radicals and further conversion to final products including CO and OH groups. The third one represents the possible channels of intermolecular crosslinks formation in the reactions of radicals recombination.

It is necessary to emphasize that VUV photooxidation process can not be reduced only to an arithmetic sum of VUV irradiation and of atomic oxygen interaction with polymer surface. Earlier [8] we studied the action of VUV (147nm) radiation and atomic oxygen on the surface of PE and PVC. It was found that the weight losses observed under the simultaneous action of VUV radiation and atomic oxygen were 2.5-3 times higher than those calculated as a sum of these two values taken from the separate experiments. We suggested that this phenomena resulted from "synergistic" effect between VUV and atomic oxygen.

4. Conclusion

The photooxidation of siloxane polymers under resonant VUV irradiation (wavelength 147nm, intensity 10^{15} quant/cm²s) in the presence of air leads to the formation of CO, OH groups and intermolecular crosslinks. The concentrations of CO and OH groups level off for irradiation times more than 30 min and reach the maximum value at 2.5 torr with the increase of air pressure in the range 0.1-100 torr. The effect of pressure on the rate of CO and OH formation closely similar to the pressure dependence of atomic oxygen

concentration at the polymer surface. This suggests that the action of atomic oxygen in conjunction with VUV irradiation is responsible for the formation of CO and OH groups. For the first approximation the photooxidation mechanism can be describe by the reaction sequence allowing for initiation, oxidation and recombination of free radicals under the action of VUV radiation O_2 and O particles. Macroradicals at the polymer surface are generated primarily by VUV irradiation and reactions with oxygen atoms. Oxidation of macroradicals and products formation occurs in the reactions with O_2 molecules. The intermolecular crosslinks via oxygen atoms are formed by the radical recombination reactions.

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