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Improvement of the micro-wear resistance of silicone by vacuum ultraviolet irradiation

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The change in micro-wear of polymers, especially a silicone rubber after vacuum ultraviolet(VUV) irradiation at the wavelength of 147 nm, was studied by means of AFM in scratching mode. It was found that the effect of VUV irradiation on polymer surface micro-wear was related to the extent of crosslinking, strongly depending on the chemical structure of polymers and irradiation conditions. The VUV treatment both in the presence of air and in vacuum resulted in a significant decrease in the micro-wear of silicone. In addition, VUV irradiation made the siloxane smoother, characterized by about a three-fold decrease in the average roughness. ESCA spectra revealed that the improvement in the micro-wear of silicone by VUV irradiation in vacuum (0.05 torr) and VUV photooxidation in air (2.5 torr) was associated with the formation of two different types of crosslinks via CH_2 groups and O atoms, respectively. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: micro-wear resistance; silicone; vacuum ultraviolet irradiation)

INTRODUCTION

It is well known that mechanical properties of polymers can be modified by crosslinking. Usually, crosslinking of polymers is performed with chemical agents, thermal treatment, and irradiation with gamma rays, UV lights, energetic electrons, and ions. Among these techniques, surface modification methods are preferable, because they lead only to crosslinking of a thin surface layer and do not alter the bulk properties of polymers. The materials after surface crosslinking will possess both the inherent flexibility of polymers and improved surface wear resistance. Recently Lee and co-authors[1–3] have shown that high energy (20–100 keV) ion beam treatment results in a substantial improvement in surface micro-hardness, wear resistance, resistance to chemicals, and electrical conductivity. They have found that the property improvements are connected with the extent of crosslinking which is responsible for formation of a three-dimensional carbon-rich network. However, this technique needs high cost ultra-vacuum equipment and an ion beam accelerator.

Effective surface modification of polymers can also be realized by irradiation of light in the short wave vacuum ultraviolet (VUV) region. Practically all polymers strongly absorb radiations with wavelength less than 180 nm which is called VUV radiation[4–6]. Xe and Kr resonance lamps with radiation wavelengths of 147.0 and 123.6 nm, respectively, and an intensity of about 10^{15} photons s^{-1} cm^{-2} can be used as a simple low-cost source of VUV radiation[7]. The characteristic depth until which VUV is absorbed depends on the polymer structure but usually does not exceed a few hundred nanometers[4]. Therefore, a dose rate of about 10^1-10^2 Mrad s^{-1} can be obtained for VUV irradiation, which is much higher than typical dose rates for ^{60}Co gamma-radiation sources (10^{-2}-10^{-1} Mrad s^{-1}) and for electron-beam accelerators in the MeV range (1-5 Mrad s^{-1}) but is comparable with dose rates of high energy ion beam accelerators (10^2-10^3 Mrad s^{-1})[1]. In terms of average linear energy transfer (LET), VUV irradiation is characterized by a value of 0.1-0.3 eV nm^{-1}, which is comparable with that for electrons in a MeV range of 0.2-0.4 eV nm^{-1}, but is less than that for ions in a MeV region (700eV nm^{-1})[1].

VUV irradiation of polymers leads to excitation of very high electronic levels near the threshold of ionization, the so-called Rydberg states. The chemistry of VUV radiation occupies the intermediate position between the chemistry of ionized states typical for ionized radiations (gamma-radiation, and electron and ion beams in the MeV region) and the traditional photochemistry of low level valence electronic states in the visible region. The energy of photons from Xe(8.4 eV) and Kr(10.0 eV) resonance lamps is enough for scission of any chemical bond in polymer molecules including C–C, C–H, C–O, C–Si, and Si–O[8]. The recombination of radicals formed after VUV photolysis can result in the formation of double bonds and crosslinks. The formation of crosslinks in polyethylene (PE), polypropylene (PP), poly(vinyl chloride)(PVC), polybutadiene, polyisoprene, and siloxane rubber under VUV irradiation at a wavelength of 147 nm was studied experimentally by Skurat and co-authors[4–10]. Thin polymer films were deposited on the surface of an MgF_2 window which is transparent to VUV radiation and then exposed to Xe lamp radiation through the window. After treatment with the corresponding solvent, the thickness of film involving only gel fraction was measured by absorption in the VUV region using a VUV monochrometer. The photoradiation yield of crosslinks was found to depend on the nature of polymers in the range of 0.1–0.7 crosslinks per 100 eV of absorbed VUV energy.

The aim of this work is to study the change in surface wear of poly(dimethyl siloxane) (PDMS) rubber after VUV irradiation by means of atomic force microscopy (AFM). To eliminate the relative change in surface micro-wear, the

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Table 1 AFM scratching depth for different polymers treated by VUV irradiation for 30 min

Polymer	Scratching depth/nm		
		VUV-treated	
	Untreated	0.05 torr	2.5 torr

Table 2 AFM scratching depth for different polymers treated by Ar plasma at 0.04 torr for 15 min

Polymer	Scratching depth/nm	
	Untreated	Plasma-treated
PDMS	99	108
PTFE	69	361
PVC	116	41

depth of the cavity formed by an AFM cantilever tip on the polymer surface in "scratching" mode was measured and then in AFM tracing mode. Only a few articles have been published with respect to AFM techniques used for testing surface micro-wear[11,12]. ESCA spectroscopy was employed to estimate the relationship between the variation in wear and the change in the chemical structure observed after VUV modification of the silicone surface.

EXPERIMENTAL

The PDMS sheet of 1 mm thickness was supplied by Dow Corning Kabushiki Kaisha (DCKK), Tokyo, Japan, and used as received. 70–120 μm thick films of PE, PVC, poly(ethylene terephthalate) (PET), and tetrafluoroethyene–hexafluoroethylene (85:15) copolymer (FEP) and 1–2 mm thick polytetrafluoroethylene (PTFE) and polystyrene (PS) were all commercial products and used after extraction with methanol.

Polymer samples of 20×25 mm^2 size were irradiated in a vacuum chamber at a residual air pressure of 0.05 torr. A resonance Xe lamp KsR-2A[7] equipped with an MgF_2 window was used. The lamp was located at a distance of 30 mm from the polymer surface. The intensity of radiation at the wavelength of 147 nm (comprising 99% of Xe lamp emission in the VUV region) measured by a "sun light blind" photodiode was 3×10^{15} photons s^{-1} cm^{-2}. As shown earlier[13,14], VUV irradiation can be also effectively used for oxidation of polymers in the presence of air. Under the irradiation conditions (sample distance and lamp intensity) of the present study, the highest rate of oxidation is predicted to appear at a pressure of 2.5 torr[15]. Indeed, photooxidation of siloxane was found to occur, resulting in the formation of crosslinks in the surface layer[15,16]. Therefore, PTFE, FEP, and PDMS were also irradiated at a pressure of 2.5 torr for comparison.

The plasma treatment of films was performed in a bell-jar-type reaction cell, Model LCVD 12 manufactured by Shimadzu Corp. Kyoto, Japan. The distance between the two electrodes was kept at 6.5 cm. The frequency and voltage applied were 5 kHz and 270 V, respectively. After fixing the films on a stainless steel sample holder placed between the two electrodes, the pressure in the bell jar was reduced to 10^{-3} torr, followed by introduction of Ar gas into the bell jar at a flow rate of 20 ml min^{-1}.

AFM was conducted with a commercial microscope (model: Olympus NV2000). Scratching of polymer surfaces was carried out at a constant force of 800 nN. An area of 5×5 μm^2 was scanned 10 times and then the depth of the cavity formed by the cantilever tip was measured in the standard tracing mode. Each sample was measured on three different points of the surface to obtain the average depth of scratching.

The change in chemical structure of the polymer surfaces was analysed by ESCA (X-ray photoelectron spectroscopy) using a model, ESCA-850V, employing Mg Kα exciting radiation. The spectra of C_{1s}, O_{1s}, F_{1s}, Cl_{2p}, and Si_{2p} peaks were scanned in this study.

RESULTS AND DISCUSSION

The results of AFM scratching for various polymers are summarized in *Table 1*. A scratching depth 0 means that the polymer could not be scratched by the AFM cantilever under the conditions employed above. As can be seen, after VUV treatment of 0.05 torr, the micro-wear directly related to the scratching depth decreased significantly for PDMS, PTFE, and PVC, decreased by about 50% for PE, and slightly increased for PS and PET. VUV treatment at 2.5 torr resulted in a significant decrease in micro-wear for PDMS, but led to about a ten times increase in wear for FEP and PTFE. Therefore, the change in micro-wear obviously depends on the chemical structure of the polymers and the irradiation conditions. It is known that PDMS can be crosslinked by VUV irradiation both in vacuum[5] and in air (2.5 torr) when effective oxidation takes place under simultaneous action of VUV and active oxygen(0^{2*}, O^3, and O species)[10]. An interesting finding observed in *Table 1* is that an effective improvement was observed for the micro-wear of PTFE after VUV irradiation. Generally, PTFE undergoes degradation during electron beam and gamma-irradiation even in vacuum[17]. Among over 20 different types of polymers (including PMMA, PS, and nylon 6,6) subjected to high-energy ion bombardment, notable exceptions to improvement in micro-wear were PTFE and polyoxymethylene, for which chain scission and degradation took place during ion implantation[1]. It was found that VUV irradiation (147 nm) of PTFE in vacuum led mainly to formation of fluoroalkyl radicals with the quantum yield of 3.1×10^{-3} [18]. According to the ESR HFS spectra analysis, the percentage of terminal radicals formed during chain scission did not exceed 10%. Probably, recombination of alkyl radicals leading to formation of crosslinks dominates chain scission during VUV irradiation. The FEP copolymer containing CF_3 side chain groups underwent degradation under VUV irradiation, both in vacuum and in the presence of air as indicated in *Table 1*.

VUV irradiation has been studied as one of the most important components in plasma–polymer interactions[19]. It was found that the primary reaction driving plasma–polymer interactions was due to the VUV radiation[20]. However, in multicomponent plasma systems, VUV irradiation of a polymer surface is accompanied by ion and electron bombardment. For a better understanding of this effect, PTFE, PVC, and PDMS exhibiting the maximum improvement in surface micro-wear after VUV irradiation in vacuum were subjected to AFM scratching after Ar plasma treatment. An Ar plasma was chosen because the emission spectrum of Ar in a gas discharge is characterized by intensive radiation appearing in the VUV region[20]. *Table 2* presents the results of AFM measurements for plasma-treated polymer samples. As can be seen, treatment with an Ar plasma is not as effective as VUV irradiation in vacuum for improving the polymer micro-wear. Probably, this is due to the destruction process on the polymer surface caused by bombardment of plasma charged particles. It should also be noted that according to our AFM measurement, Ar plasma treatment led to increased roughness for PTFE and PVC and to formation of cracks on the PDMS surface.

We carried out a more detailed study on the change in micro-wear, morphology, and chemical structure caused by VUV irradiation for PDMS which undergoes crosslinking by VUV irradiation, both in vacuum and in the presence of air, as demonstrated above. *Figure 1* shows AFM images scanned in scratching mode for PDMS untreated and VUV treated for 10 min at 0.05 and 2.5 torr. The VUV treatment improved the micro-wear of PDMS to such an extent that no cavity was formed after polymer surface scratching by the AFM cantilever. One can see from *Figure 1* that smoothing of the surface also resulted from VUV treatment. The change in scratching depth against the time of VUV treatment at air pressures of 0.05 and 2.5 torr are presented in *Figure 2*. For both pressures, the depth of scratching decreases and tends to approach zero with the irradiation time, indicating a substantial improvement in micro-wear. The rate of the process is much higher at 0.05 torr, probably because concurrence of crosslinking and degradation appeared in the photooxidation process during the initial stage of VUV treatment at 2.5 torr. *Figure 1* also revealed that the average roughness of the PDMS surface measured by AFM substantially decreased with VUV irradiation.

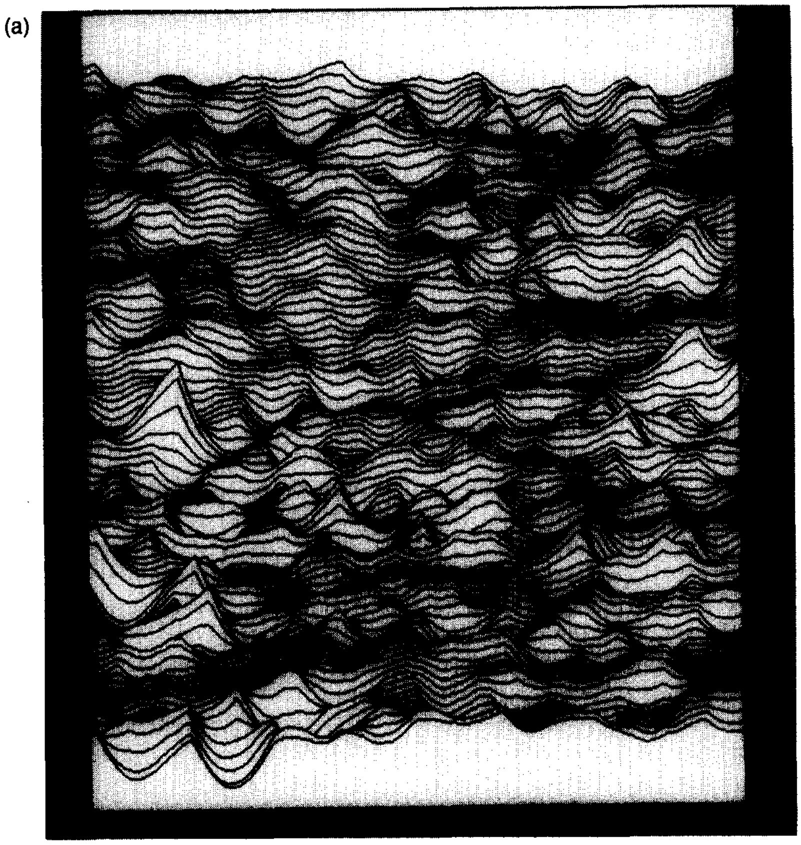
In *Figure 3*, the average roughness of PDMS determined by AFM is shown as a function of VUV treatment time. An approximately three-fold decrease of average roughness resulted from VUV treatment of PDMS, both at 0.05 and 2.5 torr. Contrary to the improvement of micro-wear, a smoothing process occurred more effectively at 2.5 torr at least when treated for about 5 min. The smoothing effect seems to have resulted from VUV etching of a weak boundary of the very surface layer of PDMS formed during fabrication. Such a surface smoothing effect was also observed for semi-crystalline polymers by scanning electron microscopy after treatment of the polymers in a low-temperature oxygen plasma[21]. Photooxidation occurring during VUV irradiation in the presence of air (2.5 torr) probably accelerated etching of the PDMS surface layer in comparison with the VUV treatment in vacuum (0.05 torr).

It is very likely that micro-wear of silicone is connected with the extent of crosslinking in the surface layer. Generally, the density of crosslinks is evaluated by measuring the insoluble gel-fraction of a polymer. In our case the thickness of the crosslinked layer was too small to determine using an analytical microbalance. The method of measuring the thickness of a crosslinked layer by VUV spectroscopy developed by Skurat and co-authors[4–6] makes it possible to measure only the gel dose but not the crosslinking density. Studying the change in ESCA spectra of PDMS after oxygen plasma treatment, Arbatskii et al.[16] have found a substantial shift in the Si_{2p} peak. Three components were used for curve fitting of the shifted Si_{2p} peak. The first one is due to the Si atom in an SiO_2 environment (102.4 eV) characteristic for the original PDMS structure; the second one is attributed to the Si atom bonded to three oxygen atoms, SiO_3 (103.2 eV), and the third one is due to the Si atom bonded to four oxygen atoms, SiO_4 (104.0 eV). The positions of these three components were previously assigned using appropriate low molecular weight model compounds containing SiO_2, SiO_3, and SiO_4 groups. Analysis of possible structures of PDMS polymer based on C, O, and Si atomic concentrations obtained from ESCA spectra has shown that the appearance of SiO_3 and SiO_4 structures indicates the formation of one and two intermolecular crosslinks via oxygen atoms, respectively. Thus, the concentration of $\equiv$Si–O–Si$\equiv$ intermolecular crosslinks can be estimated by deconvolution of the Si_{2p} peak to three peaks with the fixed position in the energy scale (102.4, 103.2 and 104.0 eV). *Figure 4* shows Si_{2p} peaks for the PDMS samples untreated and VUV-treated at pressures of 0.05 and 2.5 torr. Irradiation at 0.05 torr practically changed neither the position(102.4 eV) nor the shape of the Si_{2p} peak, indicating that modification at low pressure did not influence the original SiO_2 environment of the Si atoms. Hence, the improvement in micro-wear revealed by AFM scratching measurements can be explained in terms of crosslink formation via CH_2 groups: $\equiv$Si–CH_2–CH_2–Si$\equiv$- or -$\equiv$Si–CH_2–Si$\equiv$- types. By contrast, VUV irradiation at 2.5 torr significantly changed the position and shape of the Si_{2p} peak. The result of deconvolution shown in *Figure 4c* indicates that the band with the maximum at 104.0 eV corresponding to the structure of SiO_4 becomes the major component of the Si_{2p} peak after irradiation at 2.5 torr for 30 min. This means that during VUV irradiation in the presence of air the majority of the Si atoms were involved in intermolecular crosslinking via oxygen atoms. In addition to Si_{2p} deconvolution data, analysis of the decrease in C and the increase in O atomic concentrations obtained from ESCA spectra for the untreated and VUV-treated PDMS suggests that intermolecular crosslinking in this case can be ascribed to the -$\equiv$Si–O–Si$\equiv$- structure. The calculated number of crosslinks per 100 Si atoms formed under VUV irradiation at 2.5 torr is shown in *Figure 5* as a function of irradiation time. Comparison of these data with the time dependence of the AFM scratching depth (*Figure 2*) shows that an appreciable improvement in micro-wear could be obtained if the number of crosslinks per Si atom exceeds 0.4–0.5. The small increase in scratching depth at the initial stage of irradiation may be due to concurrence of crosslinking and degradation processes and/or removal of the weak boundary layer. This is also consistent with the rapid decrease in surface roughness during the same initial period of time (see *Figure 3*).

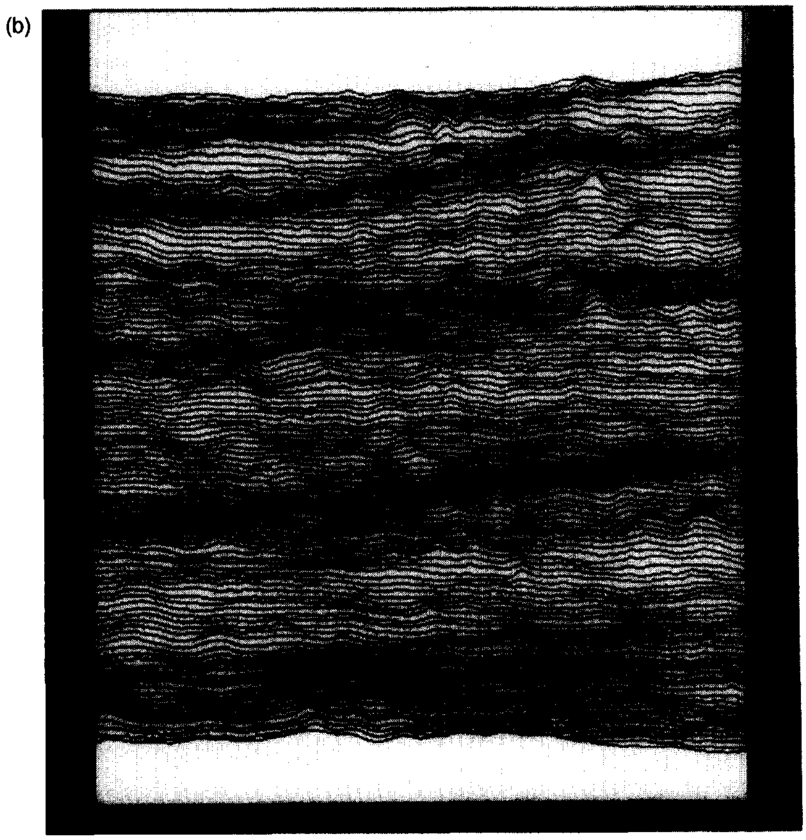
ESCA spectra of PTFE and PVC have revealed a decrease in fluorine content for PTFE (up to $F/C = 1.5$) and the almost total removal of Cl atoms from the surface layer for PVC (up to $Cl/C = 0.02$) after VUV treatment at 0.05 torr for 30 min. These data are consistent with formation of crosslinks but may also be explained by double bond formation. This is the reason why it is not possible to get quantitative information about crosslinks from the ESCA data obtained for these polymers.

CONCLUSIONS

The change in micro-wear of PDMS after VUV irradiation at the wavelength of 147 nm for PE, PS, PVC, PET, FEP, PTFE, and PDMS was studied by means of AFM in scratching mode. It was shown that the effect of VUV irradiation on surface micro-wear was related to the extent of crosslinking, strongly depending on the chemical structure of the polymer and the irradiation conditions. After VUV treatment at 0.05 torr, the micro-wear directly related to AFM scratching depth decreased significantly for



Untreated PDMS



VUV-treated PDMS (0.05 torr)

Figure 1 AFM images of PDMS untreated (a) and VUV-treated at 0.05 (b) and 2.5 torr (c) for 10 min

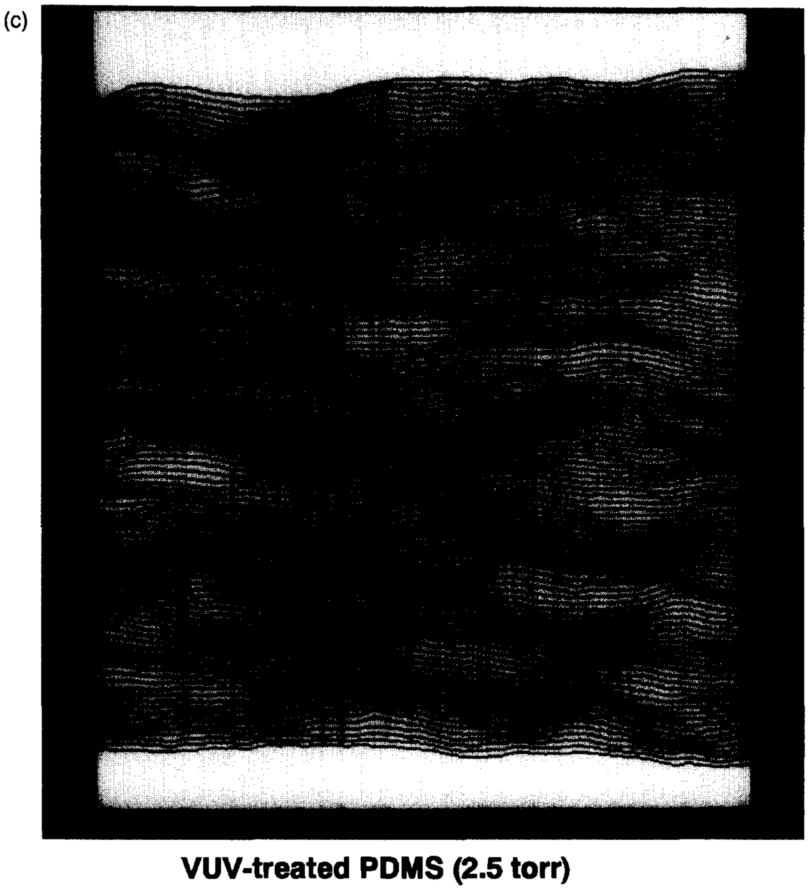


Figure 1 Continued

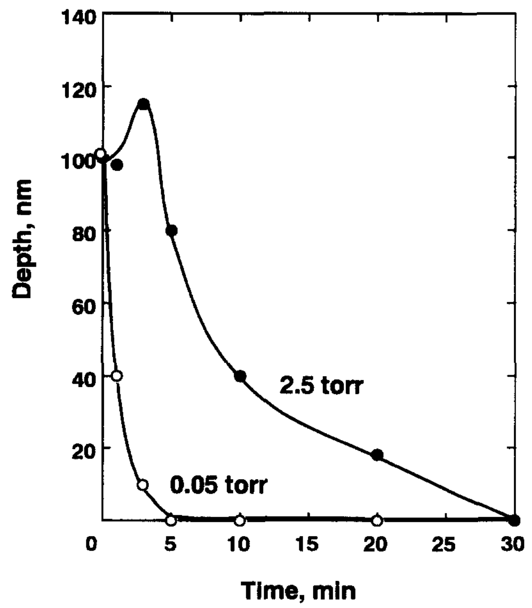


Figure 2 AFM scratching depth of PDMS as a function of VUV-treatment time: (○) 0.05 torr; (●) 2.5 torr

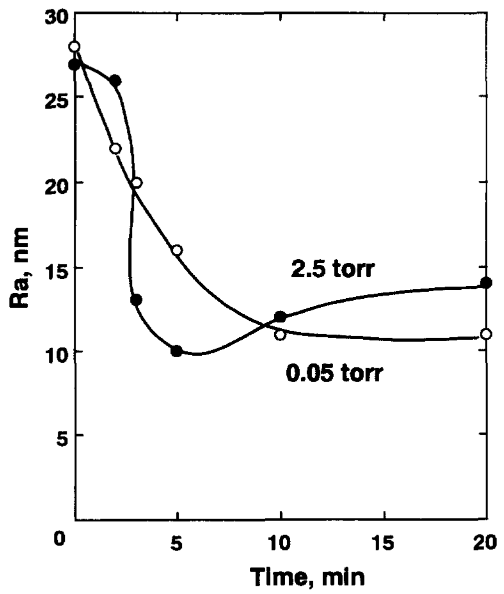


Figure 3 Average roughness (Ra) of PDMS as a function of VUV-treatment time:(○) 0.05 torr; (•) 2.5 torr

PDMS, PTFE and PVC. For PE, the micro-wear decreased by a factor of 1/2, while it slightly increased for PS and PET and increased about three times for FEP. The VUV treatment at 2.5 torr resulted in a significant decrease in micro-wear for PDMS, but at the same time led to an approximately ten-fold increase in micro-wear for FEP and PTFE.

A detailed study was carried out for PDMS which exhibited a substantial improvement in micro-wear after VUV irradiation both in vacuum (0.05 torr) and in the presence of air (2.5 torr). In addition, VUV irradiation made the siloxane surface smoother, characterized by about a three-fold decrease in the average roughness. ESCA spectra revealed that the improvement in micro-wear under VUV

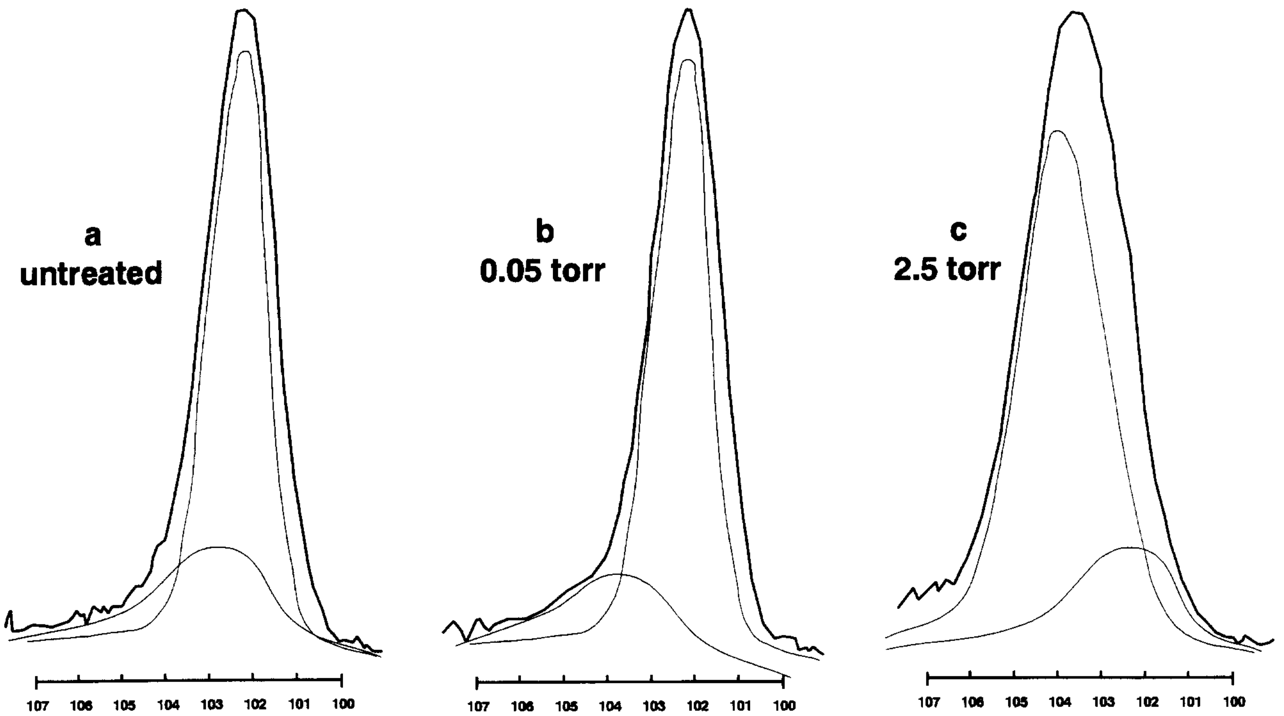


Figure 4 ESCA spectra of PDMS treated by VUV irradation of 20 min: (a) untreated; (b) 0.05 torr; and (c) 2.5 torr

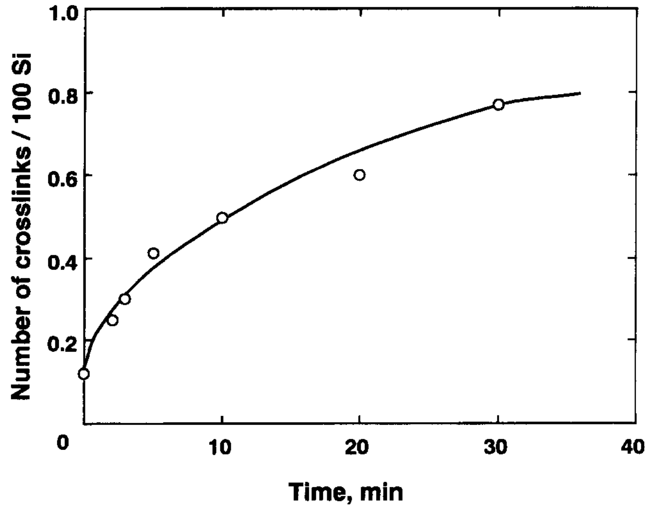


Figure 5 Number of crosslinks per 100 Si atoms for PDMS treated by VUV irradiation at 2.5 torr

irradiation in vacuum (0.05 torr) and VUV photooxidation in air (2.5 torr) was associated with the formation of two different types of crosslinks via CH_2 groups and O atoms, respectively. Comparison of the AFM data on the scratching depth with the crosslinking density estimated from the ESCA spectra showed that an appreciable improvement in micro-wear by VUV photooxidation of PDMS at 2.5 torr was observed when the number of crosslinks per 100 Si atoms exceeded 0.4–0.5. Of special note is PTFE, which is known as a degradable polymer when irradiated with ionized radiations (electron beam, gamma-radiation, and high energy ion bombardment) but can be effectively crosslinked to exhibit improved micro-wear after VUV irradiation in vacuum. Thus, irradiation with low cost and simple VUV sources, like a Xe resonance lamp, may be used for substantial improvement in micro-wear for some types of polymers.

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