

ETCHING RATES OF DIFFERENT POLYMERS IN OXYGEN PLASMA

ŠTUDIJA HITROSTI JEDKANJA RAZLIČNIH POLIMEROV V KISIKOVI PLAZMI

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Prejem rokopisa – received: 2011-10-14; sprejem za objavo – accepted for publication: 2012-02-13

The etching rates of different polymers in oxygen plasma was compared. The plasma was created in an electrodeless, radiofrequency discharge at a frequency of 27.12 MHz and a power of 200 W. The oxygen pressure was fixed at 75 Pa. The degradation of the polymers by oxidation with plasma particles was monitored by measuring the weight loss of the polymer samples. The samples were weighed just before mounting into the plasma reactor, and then again just after the plasma treatment. The following polymers were used in this study: PET (amorphous and semi-crystalline), PMMA, PS, LDPE, HDPE, PVC and PTFE. The polymer-etching rate was increasing linearly with treatment time. This was explained by the heating of the samples during the plasma treatment. The only exception was the PTFE, where the etching rate was constant. For the PVC polymer extremely high etching rates were observed. However, a characteristic of the PMMA polymer was a very low etching rate at the beginning, which was followed by an exponential increase of the etching rate with treatment time.

Keywords: polymer, etching rates, gravimetric measurements, oxygen plasma

Preučevali smo hitrosti jedkanja različnih polimerov v radiofrekvenčni kisikovi plazmi. Plazmo smo ustvarili v brezelektrodni razelektritvi s frekvenco 27,12 MHz in močjo RF generatorja 200 W. Tlak kisika med obdelavo je bil 75 Pa. Degradacijo polimera zaradi oksidacije, ki jo povzročajo plazemski delci, smo ugotavljali z meritvijo izgube mase polimernih vzorcev. Vzorce smo stehali pred izpostavo plazmi in takoj po obdelavi. V raziskavi smo uporabili naslednje polimere: amorfni in semikristalinični PET, PMMA, PS, LDPE, HDPE, PVC in PTFE. Hitrost jedkanja polimerov je linearno naraščala s časom obdelave. To smo razložili s segrevanjem vzorca med obdelavo. Edina izjema je bil polimer PTFE, kjer je bila hitrost jedkanja konstantna. Za polimer PVC smo izmerili neprimerljivo visoke hitrosti jedkanja. Značilnost polimera PMMA pa je bila zelo nizka hitrost jedkanja na začetku, nato je sledil eksponentni porast hitrosti jedkanja z naraščajočim časom obdelave.

Ključne besede: polimer, jedkanje, gravimetrične meritve, kisikova plazma

1 INTRODUCTION

Polymer materials are nowadays widely used in many different applications, especially in the food industry as a packaging material and in medicine as a suitable material for different medical devices and body implants.¹⁻⁴ The cleanliness and sterility of polymers is a very important factor in avoiding unwanted complications. While methods for the sterilization of the materials have been elaborated decades ago, and only the sterilization of very delicate components that do not withstand high-temperature treatment (i.e., polymers) represent a problem, less encouraging results have been obtained during the cleaning of components with complex shapes. This unsatisfactory cleanliness represents a problem, although a device might be sterile: the remains of dead bacteria as well as traces of body liquids or tissue often remain toxic. From this point of view it is clear that the existing cleaning techniques are far from being perfect. Even though in many cases aggressive reagents are excellent for the removal of organic residues, the application of such reagents is limited in medicine since they are usually toxic themselves. An advanced technique for the removal of organic materials that has been introduced

recently is based on the application of a heavily non-equilibrium gaseous plasma.⁸ This technique is called discharge cleaning. Reactive particles created in a gaseous plasma are capable of interacting with impurities even at low temperature.⁹ The technology is nowadays used in many branches of industry, including the microelectronics, electrical and automotive industries. Although the plasma treatment proved useful for the sterilization¹⁰⁻¹³ of simple medical devices, the wide application of non-equilibrium plasma technology is still not foreseen in medicine. The reason for this is a lack of reliable experimental data. While the interaction probabilities for a limited number of materials with gaseous plasma particles are known,¹⁴ the literature on the interaction of chemically reactive plasma particles with organic materials (blood proteins, etc.) found as contaminants on the surface of medical devices is extremely scarce.^{6,7} Furthermore, the interaction probabilities with substrate polymer materials are also important,¹⁵⁻¹⁸ if we want to avoid the surface modification and degradation of the polymers upon discharge cleaning. Namely, it is known that plasma treatment, which is usually performed in oxygen-containing gases, causes oxidation (functionalization) of a polymer material.^{14,19} This

oxidation of a polymer leads to polymer etching (material removal), which can be an unwanted effect. On the other hand, etching can be very important in some applications, like the selective etching of organic inks, where etching is used to study the distribution of pigments in an organic matrix.^{20–22} The aim of this paper is to present the results of systematic measurements of the removal rates for different polymers that are used in everyday life.

2 EXPERIMENTAL

The following polymers (from Goodfellow Ltd) were used in this study: amorphous and semi-crystalline polyethylene terephthalate (PET), polymethyl methacrylate (PMMA), polystyrene (PS), low- and high-density polyethylene (LDPE, HDPE), polyvinyl chloride (PVC) and polytetrafluoroethylene (PTFE). The chemical structure of these polymers is shown in **Figure 1**. The samples were cut into square pieces with a size of 2 cm × 2 cm to ensure a high area-to-mass ratio. Only the PVC and PMMA samples were prepared as 1 cm × 1 cm square pieces due to a shortage of the material.

Plasma etching of the polymers was performed in a cylindrical discharge tube made of Pyrex glass with a length of 0.5 m and an inner diameter of 36 mm. The system was pumped with a two-stage, oil rotary pump with a pumping speed of 16 m³ h⁻¹. The plasma was created with an inductively coupled RF generator, operating at a frequency of 27.12 MHz and a nominal power of about 200 W. Commercially available oxygen was leaked into the discharge chamber. The oxygen pressure was fixed at 75 Pa. The plasma parameters were measured with a double Langmuir probe and a catalytic probe. The plasma density was of the order of 10¹⁵ m⁻³, the electron temperature about 3 eV, and the density of neutral oxygen atoms of the order of 10²¹ m⁻³. The samples were placed on a glass holder and mounted directly to the plasma glow region.

The degradation of polymers by oxidation with plasma particles was monitored by measuring the weight loss of the polymer samples. The samples were weighed just before mounting into the plasma reactor, and then again just after the plasma treatment. A Radwag XA 110 professional microbalance was used. The accuracy of the measurements is, according to the producer, 0.01 mg.

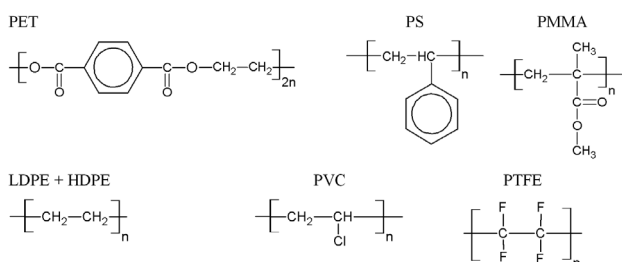


Figure 1: Chemical structure of selected polymers
Slika 1: Kemijska struktura izbranih polimerov

Samples were washed in ethanol and dried before weighing in order to remove any impurities or degradation products from the surface.

3 RESULTS AND DISCUSSION

The etching of different polymer materials due to an interaction with plasma radicals was measured. Polymer etching (material removal) is initiated by the abstraction of a hydrogen atom and the formation of a free radical.^{18,23} Polymer radical site formation affects the bond strengths in polymers and can lead to bond breaking or chain scission and thus to the formation of low-molecular-weight volatile fragments.²³ The mass loss of a polymer material after plasma treatment was measured by gravimetry and the corresponding etching rate (ξ) was calculated with the equation:

$$\xi = \frac{d}{t} = \frac{V}{At} = \frac{\Delta m/\rho}{At} \quad (1)$$

where d is the thickness of the etched layer, t is the plasma etching time, Δm is a change in the polymer mass due to etching, ρ is the polymer density, and A is the area of the polymer surface exposed to plasma. A comparison of the physical characteristics (density, melting temperature etc.) of the polymers is shown in **Table 1**. These polymers have a different sensitivity to high temperatures. Therefore, some of the polymers started to melt very quickly after turning on the

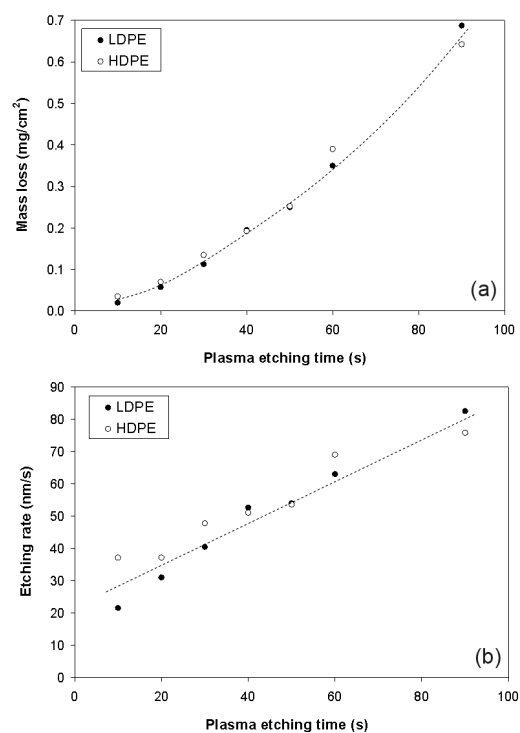


Figure 2: a) Comparison of the mass loss and b) etching rates of LDPE and HDPE polymers versus etching time

Slika 2: a) Primerjava izgube mase in b) hitrosti jedkanja polimerov LDPE in HDPE v odvisnosti od časa plazemskega jedkanja

discharge. In **Table 1** we also show the maximum working temperature as recommended by the producer and the treatment time at which the polymer melting occurred. Polymers that were treated for longer times showed a higher mass loss, which was easier to measure. Therefore, the calculated etching rates for longer treatment times are more accurate than for shorter treatment times where the differences in the polymer mass were very small.

Table 1: Comparison of the physical characteristics of different polymers and their etching rates

Tabela 1: Primerjava fizikalnih karakteristik različnih polimerov in njihovih hitrosti jedkanja

Polymer	Thick-ness (mm)	Density (g/cm ³)	Melting T/°C	Max. working T/°C	Time when melting starts	Etching rate at 20 s of treatment
PVC	0.50	1.40	100	50–75	~30 s	178 nm/s
LDPE	1.00	0.92	110	50–90	~100 s	31 nm/s
HDPE	1.00	0.95	130	55–120	~100 s	34 nm/s
PMMA	0.50	1.19	160	50–90	/	6 nm/s
PS	0.125	1.05	240	50–95	~40 s	13 nm/s
PET A	0.25	1.3–1.6	< 260	115–170	~40 s	27 nm/s
PET B	0.25	1.3–1.6	260	115–170	~100 s	35 nm/s
PTFE	0.20	2.20	327	180–260	/	18 nm/s

Figures 2 to 5 (upper figures) show the weight-loss measurements for different polymers versus treatment time. The corresponding etching rates, which were cal-

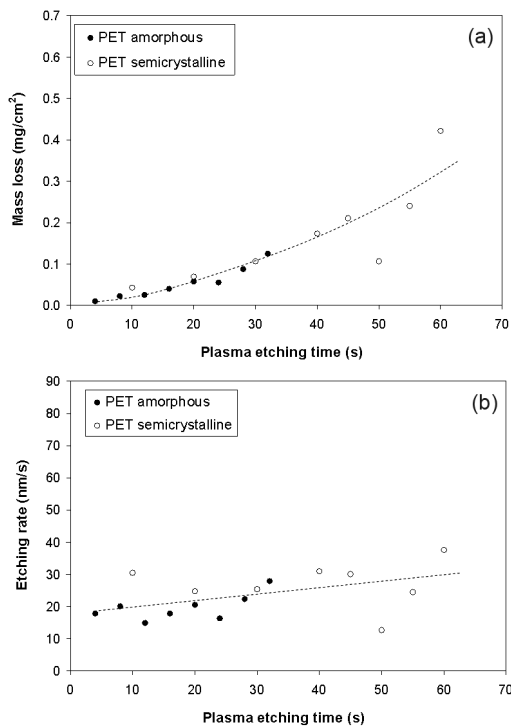


Figure 3: a) Comparison of the mass loss and b) etching rates of amorphous and semi-crystalline polymer PET versus etching time
Slika 3: a) Primerjava izgube mase in b) hitrosti jedkanja amornega in semikristaliničnega polimera PET v odvisnosti od časa plazemskega jedkanja

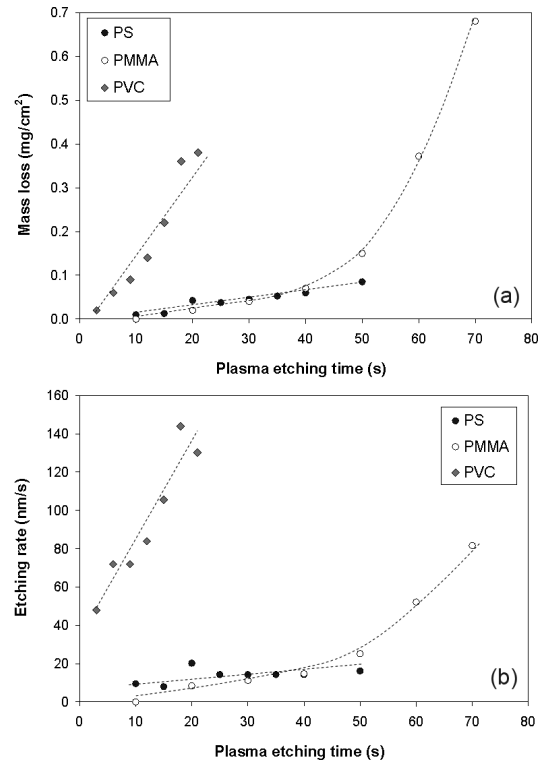


Figure 4: a) Comparison of the mass loss and b) etching rates of polymers PS, PVC and PMMA versus etching time

Slika 4: a) Primerjava izgube mase in b) hitrosti jedkanja polimerov PS, PVC in PMMA v odvisnosti od časa plazemskega jedkanja

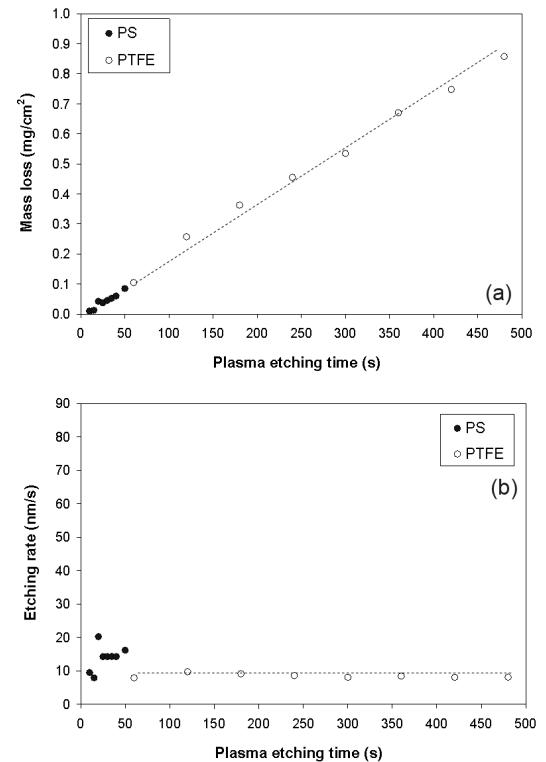


Figure 5: a) Comparison of the mass loss and b) etching rates of polymers PTFE and PS versus etching time

Slika 5: a) Primerjava izgube mase in b) hitrosti jedkanja polimerov PTFE in PS v odvisnosti od časa plazemskega jedkanja

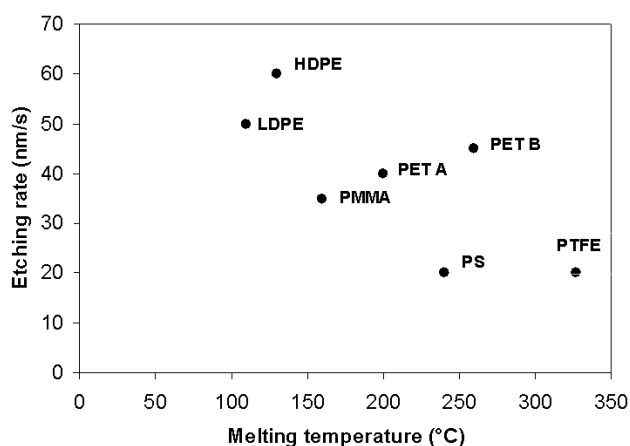


Figure 6: Dependence of the polymer-etching rate (at 60 s of treatment) on its melting temperature. Values of etching rates for some polymers were extrapolated. PET A and B refer to amorphous and semi-crystalline PET, respectively.

Slika 6: Odvisnost hitrosti jedkanja (pri 60 s obdelave) od temperature tališča polimera. Vrednosti za nekatere polimere so bile ekstrapolirane. Oznaki PET A in B se nanašata na amorfni oz. semikristalinični PET.

culated according to Eq. (1), are shown in lower **Figures 2 to 5**. In particular, **Figure 2** shows a comparison of the removal rates of the LDPE and HDPE polymers. From the upper figure we can see that there is no significant difference in the mass loss of the LDPE and HDPE polymers, although one would expect a more pronounced etching of the LDPE polymer, which has a lower crystallinity. A similar effect is observed for the amorphous and semi-crystalline polymer PET (**Figure 3**).

A comparison of the polymers PS, PMMA and PVC is shown in **Figure 4**. The etching rates of the polymer PS are similar to that of the PET and LDPE/HDPE. While for the PMMA and PVC polymers we can observe completely different behavior. Namely, for the PVC polymer we can observe an enormously high etching rate, which linearly increases with time. While for the PMMA polymer we can observe a very low etching rate at low treatment times, which after a certain time exponentially increases and becomes very high. The unusual behavior of the polymers PVC and PMMA can be explained by polymer degradation. PMMA is sensitive to oxidation and UV radiation and it may spontaneously depolymerize (i.e., after the formation of a free radical a chain-reaction mechanism starts and the polymer loses the monomer one by one). Similarly, PVC may, at elevated temperatures, release hydrogen chloride gas HCl (side-group elimination). It was also reported that chlorine-containing polymers, when treated with oxygen plasma, may modify plasma in such a way that it etches polymers at a much enhanced rate due to the presence of Cl and Cl* species.

From **Figures 2 to 4** we can conclude that the polymer-etching rate is linearly increasing with treatment time. This is probably due to thermal effects, i.e., with

increasing treatment time the temperature of the polymer also increases.¹⁴ Furthermore, a high temperature facilitates polymer degradation. In agreement with a linear increase of the polymer-etching rates with treatment time we can observe a parabolic increase of the mass loss with treatment time. This is not the case for the PTFE polymer (**Figure 5**), where we have observed a constant polymer-etching rate (independent of the treatment time) and the linear removal of the polymer material with time. The polymer PTFE is known to be chemically very inert, and therefore its surface functionalization by plasma is not very efficient.^{24–26}

When comparing the etching rates of different polymers we could not find any good correlation between the chemical structure and the polymer-etching rate. It was reported that aromatic polymers are more stable against etching in oxygen plasma^{15,23} and in our case we have found a very slow etching rate for the PS polymer. Also, the average etching rate for the aromatic PET polymer is slightly lower than for aliphatic polyethylene PE.

We have also tried to find a correlation between the melting temperature and the polymer-etching rate. The result is shown in **Figure 6**. Although we can see a general trend that polymers with a lower melting temperature have higher etching rates, the differences between the etching rates of the different polymers are not very high. Here we should also note that the values for the etching rates shown in **Figure 6** are those that polymers would have at 60 s of treatment. For those polymers that were already melted at this treatment time and for the PMMA the values were linearly extrapolated. Last but not least, the calculated etching rates at 20 s of treatment for different polymers are shown in **Table 1** as well.

4 CONCLUSIONS

The etching rates of different polymers in oxygen plasma were compared. The mass removal rate was monitored by measuring the weight loss of the polymer samples. When comparing the etching rates of different polymers we could not find any good correlation between the chemical structure and the polymer-etching rate. The polymer-etching rate was increasing linearly with treatment time. This effect was explained by the heating of the samples during the plasma treatment that facilitates the polymer degradation. The only exception was the PTFE, where the etching rate was found to be constant. For the PVC polymer, extremely high etching rates were observed. However, a characteristic of the PMMA polymer was a very low etching rate at the beginning, which was followed by an exponential increase in the etching rate with treatment time. The measured etching rates were roughly in the following order: PVC > PMMA > PE > PET > PTFE > PS.

Acknowledgement

This project was supported by Slovenian Research Agency, Project 2010/II-100 (Toward ecologically benign alternative for cleaning of delicate biomedical instruments).

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