DIFFERENCE IN SURFACE RADICAL FORMATION ON ORGANIC POLYMERS BETWEEN CW-PLASMA AND PULSED-PLASMA IRRADIATION

Masayuki Kuzuya, Shin-ichi Kondo, Takashi Sawa and Kousuke Ito

Laboratory of Pharmaceutical Physical Chemistry, Gifu Pharmaceutical University.

5-6-1, Mitahora-Higashi, Gifu 502-8585, Japan

e-mail: kuzuya@gifu-pu.ac.jp

Abstract

The nature of free radical formation by pulsed-plasma irradiation was studied on several selected organic polymers in its comparison with those of continuous wave(CW)-plasma irradiation based on the measurement of electron spin resonance(ESR)spectra.

7. Introduction

There has recently been increasing interest in applications of a pulsed plasma for thin film formation in a plasma polymerization. It is a well known fact that the film composition in continuous wave (CW)-plasma polymerization varies in a highly non-linear fashion with not only intensive properties (concentration, temperature, pressure etc.) but also various extensive properties (discharge power, volume and intensity of plasma, shape & size of plasma reactor etc). As a result, plasma polymerization is composed of complicated processes that are not amenable to a simple rationalization, and plasma polymerized thin films produced are generally of highly cross-linked network.

On the other hand, pulsed plasma can provide an opportunity to generate plasma-polymerized thin films under unusually low total power input, and to produce more discrete thin films with high retainment of structures of starting monomers. The pulsed-plasma power equivalent to CW-plasma (Weq) is known to be calculated as follows:

\[ \text{Weq} = \ast \text{on} \ast (\ast \text{on}^{+} \ast \text{off}) \ast \text{peak power.} \]

where * on and * off are the plasma on and off times, and peak power is the power inputs during the plasma on periods of the pulsed cycle. Thus, the averaged power inputs under pulsed plasma is significantly lower than those under CW-plasma conditions.

Several authors have recently reported the studies on plasma polymerization using pulsed plasma. For instance, Timmons et al have reported that the effect of duty cycles of pulsed plasma on polymer film compositions. Relatively linear polymers where the monomer structure retains with a high level in the film composition were obtained as the plasma duty cycle employed during film formation was decreased. They have also reported that an increased energy efficiency was observed in film formation rates as the duty cycle is decreased.[1] This fact has been interpreted in terms of the fact that the significant film formation occurred during plasma-off times under pulsed plasma conditions.
There is a growing body of literature concerned with plasma treatment of polymer surfaces, several of which treatments have reached the stage of commercial development. In view of the fact that surface reactions of plasma treatment are initiated by plasma-induced surface radicals, study of the radicals formed is of utmost importance for full understanding of the nature of plasma treatment. Thus, we have undertaken a number of plasma-irradiation on a wide variety of polymers, synthetic and natural, and the surface radicals formed were studied by electron spin resonance (ESR) coupled with the aid of systematic computer simulations.[2]

However, the nature of free radical formation under pulsed-plasma conditions has not yet been studied. It is expected that pulsed-plasma irradiation will generate the difference in the nature of free radical formation on the polymer surfaces, since pulsed-plasma irradiation can significantly reduce the effect of the heating on the polymer surfaces due to lower averaged power inputs.

With a view of gaining more information about the nature of plasma treatment and pulsed plasma polymerization, and providing a further effective basis for the future experimental design, we have undertaken for the first time the ESR study on surface radical formation of several kinds of polymers under pulsed-plasma conditions. We have selected several organic polymers for the present study of which radicals generated by CW-plasma irradiation have been previously characterized.

In this contribution, we present the ESR study on the nature of surface radical formation of several aromatic ring-containing polymers such as polystyrene(PST), polyethylene terephthalate(PET) and polycarbonate (PC) and polyethylene, high-density(HDPE) and low-density (LDPE), and cellulose (CE) as a representative natural polymer, by pulsed-plasma irradiation with several operational variables of the averaged power inputs and duty ratios in its comparison with those by CW plasma irradiation.

8. Experimental Section

Method of Plasma Irradiation. Powdered samples (100 mg) were placed in a specially designed ampule (30 mm i.d., 100 mm long) with a capillary tube (2 mm i.d.) at the uppermost part. The ampule was filled with argon gas for plasmolysis (0.3 Torr) and sealed. Then the plasma state was sustained for the prescribed period of time with agitation of samples at room temperature by a radio frequency discharge of inductive coupling using four-loop antenna at 13.56 MHz with the prescribed supplied power. Pulsed plasma irradiation was carried out according to the method similar to the above using the radio frequency generator connected with a pulse generator under the prescribed plasma on and off pulse widths in the millisecond range as a duty cycle. The ESR measurements were preformed while turning the ampule upside down after plasma irradiation at appropriate intervals, which is fundamentally the same procedure as that reported earlier.[2]

ESR Spectral Measurement. ESR spectra were recorded by a JES-RE1X (JEOL) spectro-meter with X-band and 100 KHz field modulation. Care was taken to ensure that no saturation occurred and that the line shape was not distorted by excessive modulation amplitude. From a plot of the square root of the microwave power versus the signal peak height, a microwave power level of 0.01 mW was chosen. The ESR spectral intensity was determined by double integration. The radical concentration (spin numbers/g) was calculated from the spectral intensities with the aid of calibrated lines obtained from the spectral intensities of PMMA(poly(methylmethacrylate) sample impregnated with DPPH. Measurements of g-values were made relative to the fourth signal from the lower magnetic field (g=1.981) of Mn²⁺ in MgO.

234
9. Results and Discussion

Observed ESR Spectra of Plasma-Irradiated Polymers. Figure 1 shows the representative observed ESR spectra of pulsed plasma-irradiated polymers at a power input of 20W with a fixed duty cycle of 0.5 (1ms on and 1ms off) equivalent to the averaged power input of 10W together with those of CW-plasma irradiated polymers at a power input of 10W.

It is seen from Figure 1 that the comparison between pulsed plasma and CW-plasma did not show much difference in the spectral features from each other under the present operational conditions, but the spectral features appear to differ from each other in the case of PST and cellulose, i.e., the relative intensity of the lateral peak intensity of the triplet-like spectra in the pulsed plasma irradiation is appreciably larger than that in the CW plasma irradiation.

We have shown in Fig.2 the progressive changes in the observed ESR spectra of plasma-irradiated PST at a higher fixed peak power input of 100W with variable plasma duration as a representative example.

Fig. 1  Representative ESR spectra of several organic polymers (a) CW plasma-irradiation at a power input of 10W and (b) pulsed plasma-irradiation at peak power input of 20W with a fixed duty cycle of 0.5 (1ms on/1ms off) (Weq; 10W).
Fig. 2 Progressive changes in ESR spectra of PST at a fixed peak power input of 100W. (A): CW plasma, (B): pulsed plasma with a fixed duty ratio of 0.5 (1ms on/1ms off).

It is apparent that, although the total spectral intensity is lower in a series of pulsed plasma irradiation (B) than those in CW plasma irradiation (A) due to the lower averaged power input of pulsed plasma irradiation (Weq : 50 W), the ratio of lateral peak intensity to the central peak intensity in a series of (B) is higher than in those of (A).

Since the ESR spectra of plasma irradiated PST is known to be composed of two kinds of radicals, cyclohexadienyl radicals (1)(formed by a random addition of hydrogen to the aromatic ring), showing a triplet-like spectrum due to admixture of several cyclohexadienyl radicals, and immobilized dangling bond site (2) located in the crosslinked network, exhibiting a broad singlet-like spectrum, the ratio of peak intensity in the central peak to that of the lateral peak can provide an indication of the radical composition, (1) and (2).

Thus, we have estimated the ratio by measuring each of the peak height of the observed

Table 1. Ratio of peak height (b/a) of the central peak (b) to the lateral peak (a) in PST.

<table>
<thead>
<tr>
<th>Plasma duration</th>
<th>CW 100W</th>
<th>Pulsed (1ms/1ms) Peak power 100W</th>
</tr>
</thead>
<tbody>
<tr>
<td>15s</td>
<td>2.12</td>
<td>1.78</td>
</tr>
<tr>
<td>30s</td>
<td>2.55</td>
<td>2.05</td>
</tr>
<tr>
<td>60s</td>
<td>3.10</td>
<td>2.48</td>
</tr>
<tr>
<td>120s</td>
<td>3.91</td>
<td>3.13</td>
</tr>
<tr>
<td>180s</td>
<td>4.73</td>
<td>3.54</td>
</tr>
</tbody>
</table>

236
spectra and the result was listed in Table 1. It became clear that the ratio of the lateral peak is more intense in (B) by 20-30% than that in (A), and such a ratio gradually increases as the plasma duration increases. We have already demonstrated that the crosslinking reaction involving the radical (I) are very susceptible to the temperature.[11] Thus, the result may have been rationalized in terms of such that pulsed plasma irradiation has suppressed the effect of heat fusion on the polymer surface.

Figure 3 shows the progressive changes in the total spectral intensities of pulsed plasma irradiated PST at an equivalent power input of 30W with various duty cycle. It is seen that the radical formation was nearly proportional to the duty cycle of pulsed plasma; the radical formation decreased as the value of duty cycle decreased indicating that the pulsed plasma does not improve the energy efficiency in the radical formation under the present operational conditions. This is in a contrast to those of plasma polymerization under pulsed plasma conditions where the thin film formation occurs during plasma-off time.

![Graph showing progressive changes in spectral intensities of pulsed plasma-irradiated PST at an equivalent power input of 30W with various duty cycles (on/off time in ms).](image)

**Fig. 3** Progressive changes in spectral intensities of pulsed plasma-irradiated PST at an equivalent power input of 30W with various duty cycles (on/off time in ms). (●) 0.6/1.4, 100W; (○) 1/1, 60W; (▲) 1.5/0.5, 40W, (□) CW, 30W.

**Conclusion**

Although pulsed plasma can provide a powerful and effective method to permit a high retention of monomer structures in plasma polymerized thin film formation with high energy efficiency, it exhibited only an small change in both amount and structure of the surface radicals in many polymers examined under the present operational pulse conditions. It can be understood that the radical formation does not occur during the plasma-off times so that pulsed plasma did not improve the energy efficiency in the radical formation. From the present result, it can be expected that the radical components formed on the polymers during pulsed plasma irradiation could be largely changed on its comparison with those during the conventional CW-plasma irradiation by selecting the pulse conditions such as the larger plasma on and off pulse widths.
References

6612-6617
Soc., 114 (1992), 6505-6512.
11301-11307.
79-89.
(1998), 3225-3229.
3234.