

Investigating the Plasma Surface Modification of Polystyrene at Low Ion Power Densities

Marshal Dhayal,[†] Kristina L. Parry,[‡] Robert D. Short,[‡] and James W. Bradley*

Department of Physics, UMIST, Sackville Street, Manchester, M60 1QD United Kingdom, and Department of Engineering Materials, University of Sheffield, Mappin Street, Sheffield S1 3JD, United Kingdom

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A new grid-separated, two-chamber low-pressure plasma reactor [Dhayal, M.; Forder, D.; R. Short, D.; Bradley, J. W. *Vacuum* **2003**, 70, 67]¹ has been developed to study the surface modification of polymeric materials under low ion power density bombardment. Through external biasing of the grids, the ion flux Γ and energy E of the bombarding plasma ions at the substrate can be controlled independently (within certain experimental limits). Importantly, this can be achieved without changing the VUV component of the plasma. In the present arrangement, ion power densities ($q\Gamma E$) in the range 0.7–15.5 W m⁻² can be achieved. This allows a low power density regime to be explored, not possible in typical glass barrel RF reactors often used for surface modification of polymeric materials, in which ion power densities are typically 10–160 W m⁻². The effect of ion energy and flux on the surface modification of polystyrene (PS) was quantified by the ratio of atomic oxygen to carbon in the post-treated samples exposed to air (measured by X-ray photoelectron spectroscopy, XPS). It was found that, over the whole available range in ion fluxes, ($1.7\text{--}5 \times 10^{18}$ m⁻² s⁻¹) and energies (1.5–23 eV), the O/C ratios did not change with O/C about 0.1 to 0.12 for plasma exposure times of 90 s. With elimination of the ion species from the processing region of the discharge through grid biasing, the O/C ratios were also found not to change, indication that below a certain threshold of ion power (at least 15.5 W m⁻²) ions play little role in the surface modification. By replacing the grids with a LiF window (cutoff wavelength λ_c 104 nm) having a transparency in the VUV region (<200 nm) at least as good as the geometric transmission area of the two grid system we observe again little change in O/C, indicating that the dominant species in production of free radical sites is the VUV, with any excited neutral species and radicals in the plasma playing a minor role.

1. Introduction

The low-pressure (0.1–10 Pa) RF plasma treatment of polymeric materials has become an attractive method to modify the surface properties (without affecting bulk material), providing, for instance, enhanced wettability, printability, and adhesion etc.² Due to the mobile nature of plasma species, the ions, electrons, neutrals, and free radicals (and photons), plasma treatment can be used on objects of complicated geometry.

Despite the burgeoning literature on plasma treatment,² there is little agreement on the relative importance of the different mechanisms involved in the plasma-polymer surface interaction. This confusion arises because reactors used are not designed with the systematic investigation of plasma parameters in mind. Widely employed over the past 25 years, in academia and to a lesser extent in industry, has been the tubular glass reactor (see Clark and Dilks³).

This plasma reactor design, despite its continuing popularity, has been poorly characterized, and for research purposes, the competing physical phenomena (such as ion and VUV bombardment, contributing to surface bond breaking) cannot easily be differentiated from each other in terms of their contribution to the process. The role of ions in plasma treatment has been “hotly” debated, without much serious experimental evidence. Lack of data stems from a poor knowledge of ion fluxes/

energies/identities (in the plasma), although some attempts have been made to measure the energy flux of the ion and VUV species bombarding isolated polymer substrates, for instance in capacitively coupled RF argon plasma.⁴

The presence and effect of the VUV component in low-pressure reactors used for surface modification have been studied extensively. For instance, Clark and Dilks⁵ showed that in an argon gas RF coupled plasma the most intense VUV lines were at 104.8 and 106.6 nm corresponding to Ar (I) transitions of the neutral atoms ($3p^5 4s \rightarrow 3p^6$). In the region studied (65–110 nm) the intensity of these lines was 2 orders of magnitude greater than the total output of the remainder of the spectrum. Furthermore these intensities increased 3-fold as a function of input power (2 → 20W) and maximized at a gas pressure of 0.65 Pa. Egitto and Mateinzo⁶ used a series of UV transmitting crystals and XPS valence band analysis to show that photo-ionization took place when photons with energies greater than the first ionization potential of the polymer were absorbed by the sample. Contact angle measurements were used to study surface changes and they found that modification of polyethylene (PE) occurred with photon energies greater than 8 eV and polytetrafluorethylene (PTFE) with photon energies greater than 10 eV. Shard and Badyal⁷ compared VUV ($\lambda < 200$ nm) radiation from a nitrogen plasma transmitted through a LiF window with an oxygen plasma and found similar modification produced by the two in samples of PS, PE and polyetheretherketone (PEEK). The VUV treatment of PE has been studied by Holländer et al. in a number of papers. They observed increases in the PE surface O/C ratio after several minutes of exposure

* To whom correspondence should be addressed. E-mail: j.w.bradley@umist.ac.uk.

[†] UMIST.

[‡] University of Sheffield.

to the VUV emission of a microwave plasma discharge operating in a number of gases.⁸ The sample compartment was separated from the plasma by a magnesium fluoride window (cut off wavelength $\lambda_c = 112$ nm), and exposure times ranged up to 1 h. In conclusion, the formation of radicals by VUV irradiation appeared to be an important initiation step leading to a high rate of oxidation, whereas attack by oxygen atoms occurred at a much slower rate. However, much of the VUV emission was excluded with the magnesium fluoride window. A further study concluded that modification from the VUV component of a gas plasma depended strongly on the nature of the discharge, and correlated with the mean intensity of the VUV peaks in the spectrum in the order H_2 plasma > N_2 plasma > O_2 plasma > He plasma.⁹ However, Groning et al.¹⁰ used low-energy ions (including reactive O_2 and N_2 plasma ions and ion beams at energies <10 eV) together with separate VUV lamp irradiation to show that much of the chemical modification of poly(methyl methacrylate) (PMMA) was predominately due to ions, and that low energy ion-surface interactions are key in the modification process.

In the current study, we use a specially developed grid-separated two-chamber discharge to investigate the effect of ion energy and flux at low levels of power input at the substrate in the modification of thin film polystyrene surfaces. In contrast to previous experiments on the effect of VUV, in which a VUV transparent window separates the plasma and substrate, the device, through grid biasing, allows us to eliminate the ionic component from the modification process but leave unchanged the VUV component at the surface. In this way, we can study better the individual effect of the ionic and vacuum ultraviolet photon (VUV) component in the plasma on the modification process. We see this as the first step in the pursuit of a reactor, in which the energy and flux of the species can be tailored and the role of each on the surface modification better quantified. Conventional RF (wire wound capacitively coupled) barrel reactors for processing polymeric materials are characterized by relatively high ion bombarding energies (10–100 eV) and fluxes ($1\text{--}10 \times 10^{18} \text{ m}^{-2} \text{ s}^{-1}$)¹¹ giving relatively high power densities to the polymeric surface, for instance up to 160 W m^{-2} . Consequently, in the regime where the ionic component is a significant factor in the modification plasma, treatment times are very short, for instance only 1–2 s, to achieve maximum surface modification (saturated number of free radical sites).^{12,13} Here, in our discharge, low ion power densities can be obtained, which also allows us to investigate more easily the role of VUV photons in the modification process. In this investigation, we treat polystyrene thin films for a set period of time (90 s) for a range of ion fluxes and energies, controlled through variation of the potential on fine metallic grids, which divide the discharge into two parts. This has the advantage over the barrel reactor, since it is not necessary to alter the gas pressure or discharge power to achieve independent variation in the charged particle concentrations and energies.

2. The Experimental Arrangement

A schematic diagram of the two-stage radio frequency (RF) driven plasma reactor used in this study is shown in Figure 1. The turbo molecular pumping system allowed base pressures of less than 10^{-5} Torr to be achieved and therefore low levels of impurity species in the discharge, for instance, less than 1% of that found in glass barrel reactors pumped by a single rotary pump.^{3–5} The source characteristics and operation are described in detail in ref 1. In all of the studies carried out here, the argon gas pressure was fixed at 2.6 Pa (20 mTorr). The substrate

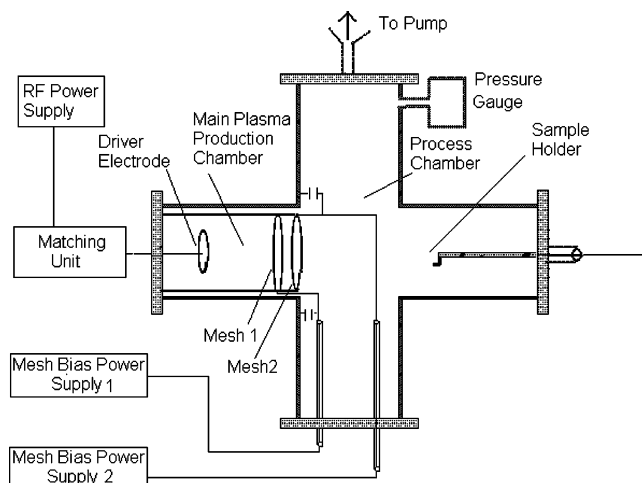


Figure 1. Schematic diagram of grid-separated RF plasma discharge together with the sample holder arrangement.

position, relative to the last grid, could be varied from 15 to 70 mm. The PS samples were placed in the process chamber with their upper surfaces facing into the main RF plasma source. Dividing the plasma using two such fine grids allow (in non polymerizing plasmas at least) the plasma density (N_e) and electron temperature (kT_e/e) in the downstream process plasma to be controlled. For instance, by applying dc potentials V_{mesh1} and V_{mesh2} , in the range -20 to $+20$ V, to the two grids, N_e and T_e in the process chamber can be varied, (with this particular design), from about 10^{14} to $5 \times 10^{15} \text{ m}^{-3}$ and 0.2 to 5.5 eV respectively.^{1,14} Since the plasma in the processing chamber is essentially collisionless and there is no RF excitation in that region, the value of T_e will determine the mean ion bombarding energy, with $E = e(V_p - V_f) \sim 5kT_e$ where V_p and V_f are the plasma and floating potentials.¹⁵ In this regime the ion flux is $\Gamma \sim N_e \sqrt{kT_e/M}$, and therefore, we see that through variation of N_e and T_e that E and Γ can be controlled independently.

The important plasma parameters in the process chamber, namely the ion saturation current ($q\Gamma_i$), electron density N_e , and temperature T_e , floating V_f and plasma V_p potentials were determined using a Langmuir probe in a previous study.¹ The ion power density at the surface is defined as $P = q\Gamma E$ (W m^{-2}) where q is the electronic charge on the ions.

In a preliminary set of experiments, we have determined that for grid biases of $V_{\text{mesh1}} = +10$ V and V_{mesh2} more negative than -60 V, no plasma (ions or electrons) is transmitted through the grids to the process chamber. However, each grid has a transparency (projection of open to closed area) of 45%, and therefore, clearly both photons and excited neutral species from the main RF plasma can bombard the substrate.

In a separate experiment a LiF window (cut off λ_c 104 nm) of 6 cm diameter, replaced the grid system. This allows irradiation of the polymer surface by photons (including VUV photons) only, eliminating all other particle species. The transparency of the window as a function of wavelengths λ was unknown, however, it was certified $> 10\%$ for $\lambda < 150$ nm.

3. Results and Discussion

3.1. Polymer Surface Modification with Ion Control. In this study, thin spin cast circular polystyrene samples (of diameter 1 cm) were plasma treated for 90 s, for a range of ion energies and ion fluxes obtained through grid electrical biasing. The substrate was located 15 mm from the second grid. This included treatment in the absence of charged species, and also neutrals (i.e., by VUV photons only). Post-treated samples were

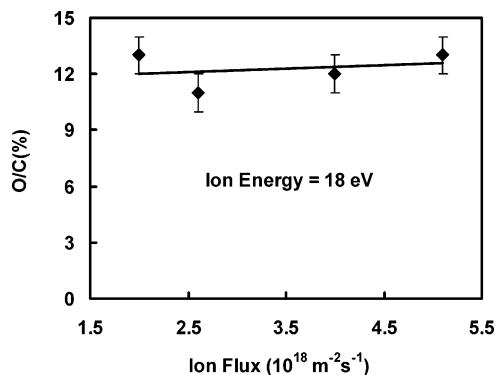


Figure 2. Atomic oxygen-to-carbon ratio (O/C) plotted as a percentage against the ion flux at a constant ion energy of 18 eV. The sample position was 15 mm from the second grid and the pressure was 2.6 Pa, the main plasma RF power was 20 W.

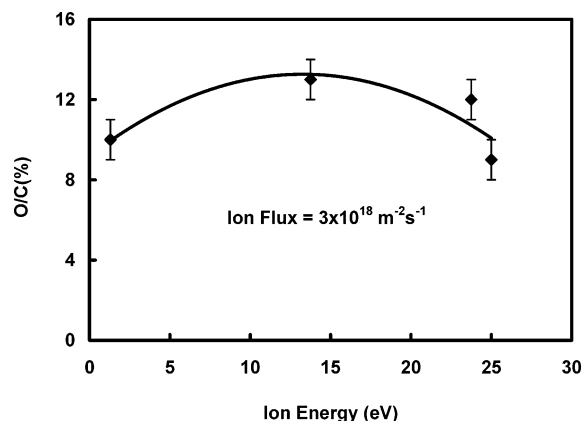


Figure 3. Atomic oxygen-to-carbon ratio (O/C) plotted as a percentage against the ion energy at a constant ion flux of $(3 \pm 0.4) \times 10^{18} \text{ m}^{-2} \text{ s}^{-1}$. The sample position was 15 mm from the second grid and the pressure was 2.6 Pa, the main plasma RF power was 20 W.

exposed to atmospheric oxygen and the level of surface modification quantified from a measure of the atomic oxygen-to-carbon ratio (O/C) in the upper level, determined by XPS (VG CLAM 2 spectrometer) fitted with a Mg KR X-ray gun.

Figure 2 shows the effect of varying the ion bombarding flux at constant ion energy (in this case $E = 18 \text{ eV}$) on the level of surface modification. The main plasma power was 20 W. Despite the increase of a factor of 3 in Γ (from 1.7 to $5 \times 10^{18} \text{ m}^{-2} \text{ s}^{-1}$), the O/C ratios are constant at about 0.12. This insensitivity to changes in the plasma conditions is also seen with variation of the ion energy E for a constant flux ($3 \times 10^{18} \text{ m}^{-2} \text{ s}^{-1}$) in Figure 3. For bombarding energies in the range 1.5–23 eV, the O/C ratios do not change appreciably, with O/C again about 0.12. However, it was noted that for further increases in the ion energy up to 25 eV, the O/C ratio was reduced by about 20% from its maximum value. We believe this may be due to ion etching of the surface, as discussed in ref 7. In the current experiment arrangement it was not possible to achieve ion energies in excess of 25 eV while holding a constant ion flux.

The data represented in Figures 2 and 3 can be combined to allow a plot of O/C against ion power density ($P = qE\Gamma$). Although P varies in the experiment, from 0.7 to 15.5 W m^{-2} , of course, no variation in the surface modification is measured for this range, as demonstrated in Figure 4. At the highest power density (15.5 W m^{-2}) a plasma treatment time of 90 s corresponds to an ion energy density of 1500 J m^{-2} . Surprisingly, this is a much higher value than the energy density (165 J m^{-2}) required to produce the same oxygen functionality (O/C

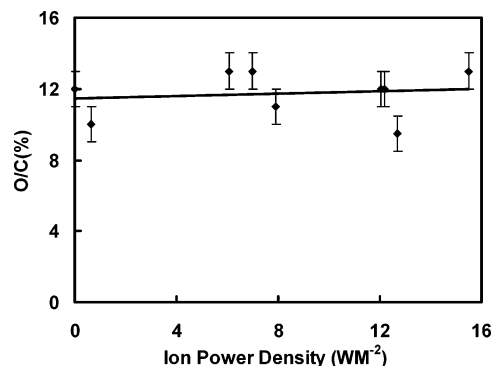


Figure 4. Atomic oxygen-to-carbon ratio (O/C) plotted as a percentage against ion power density. The sample position was 15 mm from the second grid and the pressure was 2.6 Pa, the main plasma RF power was 20 W. The point corresponding to zero ion power density (obtained through mesh biasing) is taken from Figure 5.

$= 0.12$ in PS) in the conventional glass barrel reactor.^{4,12,13} As discussed in ref 4, the ions contributed 35 W m^{-2} , out of a combined total power density (ion and VUV) of 70 W m^{-2} , giving rise to $\text{O/C} = 0.12$ after only 5 s plasma exposure time. Comparison between these previous results and those here may suggest that below a certain threshold power density, ions have little or no effect on the polymer, irrespective of the treatment time.

3.2. Polymer Surface Modification with Elimination of the Ion Flux. The independence of O/C with ion energy or flux indicates that at these low ionic power densities at the surface (i.e., 15.5 W m^{-2} or below) ions play little role in the modification process. Therefore, a further study was carried out to eliminate completely the charged particle species from the process chamber. This allowed us to investigate the effect of VUV and any excited neutral species (the latter may include metastable argon, $4\text{S } ^3\text{P}_0$ and $4\text{S } ^3\text{P}_2$ states with energy 11.7 and 11.5 eV respectively). To eliminate both electrons and ions from the process vessel bias voltages of $V_{\text{mesh1}} = 10 \text{ V}$ and $V_{\text{mesh2}} = -60 \text{ V}$ were applied. This technique has the benefit of not altering the main discharge conditions, and therefore, the photon/neutral bombardment characteristics remain unchanged even though the ion flux to the surface is “switched off”. We estimate that the two-mesh system attenuates the photon flux from the main chamber by about 80%. In these experiments, the main RF discharge power was also varied (from 5 to 30 W) to investigate qualitatively the dependency of O/C on the intensity of the flux of photons transmitted through the grids. Unfortunately, the absolute flux and energy fluxes of the VUV photons in the process chamber, falling on the sample, could not be determined, as was achieved in ref 4.

In an extension to the study, the grid system was the entirely replaced with a high transparency LiF window. This had the effect of isolating the ionic and neutral species completely from the process chamber, while allowing transmission of the photon flux (at least 10% at wavelengths $< 150 \text{ nm}$), i.e., a similar transmission to the grids, at these energetic wavelengths.

Figure 5 shows the measured O/C ratios as a function of main discharge power (5 to 30 W) for two different modes of treatment: 1) combined photonic and neutral bombardment, achieved through grid biasing and 2) photon (including VUV) bombardment alone, achieved using the LiF window. We see that in the first case the O/C ratios increases from 0.08 to 0.16 with increasing power; however, at 20 W, there is no appreciable difference with the results in Figures 2 or 3. That is, the total elimination of the ionic flux makes no difference to the level of treatment in this regime. In the second case, with the added

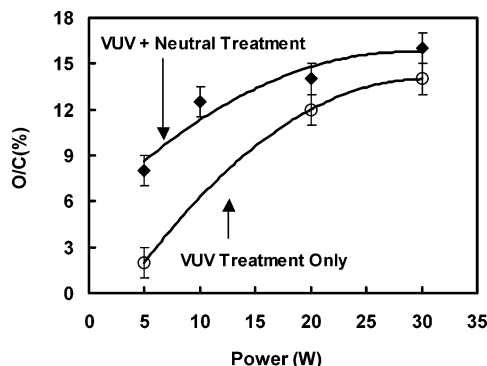


Figure 5. Atomic oxygen-to-carbon ratio (O/C) plotted as a percentage against main RF discharge power for two different cases. (1) Diamonds: total ion elimination by selective mesh biasing ($V_{\text{mesh1}} = 10$ V and $V_{\text{mesh2}} = -60$ V). (2) Circles: VUV selection only by use of a LiF VUV transparent window. The sample position was 15 mm from the second grid and the pressure is 2.6 Pa.

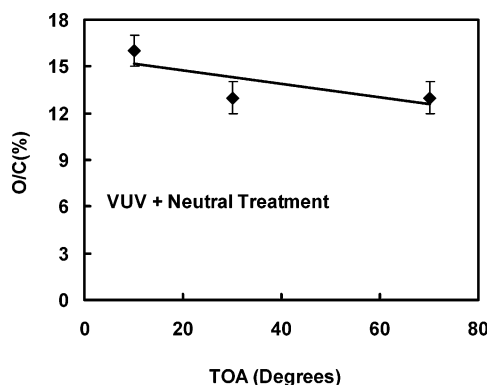


Figure 6. Atomic oxygen-to-carbon ratio (O/C) plotted as a percentage against take-off angle for VUV and neutral treatment (i.e., in the absence of ions). The sample position was 15 mm from the second grid, the pressure was 2.6 Pa and the main plasma RF power was 20 W. The uniformity with depth indicates the treatment is predominately from VUV photons.

elimination of the neutral species, the O/C ratios are somewhat lower, varying from 0.02 to 0.13. However, comparing the two curves in Figure 5 directly is difficult since the window and grids will have different transmission to photons and the presence of the window may change the main discharge conditions (not recorded). Despite, the lack of a quantitative comparison, we see from figures 2, 3 and 5 that in this discharge, treatment through photon bombardment appears to dominate the process. To investigate the uniformity of treatment with depth, a number of the PS surfaces were analyzed by XPS over a range of take-off angles, from 10 to 75°. The results for samples treated in the absence of all charged species (i.e. through photonic and neutral species bombardment) are shown in Figure 6. The O/C ratios are found to vary little with angle, indicating a uniformity of treatment through the top 50 ns of the surface, and therefore predominantly VUV initiated production of free-radical sites,¹⁶ rather than through energy exchange with excited neutral species.

It is interesting that in this discharge we can achieve a peak ratio of O/C of 0.15 in the treated films after 90 s plasma exposure time, whereas this level of modification could only be achieved in time periods of 15 to 60 min in other plasma based VUV sources.^{17–19} This may be due to an effective collimation of the photon flux from source to process chamber, not seen elsewhere, giving rise to a very efficient VUV source for processing. To investigate further the characteristics of the

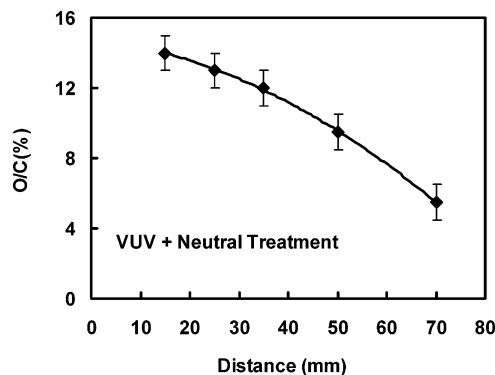


Figure 7. Atomic oxygen-to-carbon ratio (O/C) plotted as a percentage against sample distance for VUV and neutral treatment (i.e., in the absence of ions). The pressure was 2.6 Pa and the main plasma RF power was 20 W.

source, PS samples were treated at different positions downstream (15–80 mm) in the absence of charged particles using selective grid biasing, i.e., with the main plasma acting predominately as a photonic source. The results are shown in Figure 7. We infer from Figure 5 that excited neutral species have (in this arrangement) little effect on the level of surface modification compared to that of VUV photons. With increasing distance, 15–70 mm, there is a 50% decrease in the O/C ratio from 0.14 to 0.06. However, if the plasma acted as a point source of photons with the center at the midpoint of the main chamber, a much larger drop could be expected. A spherical expansion of photon flux (a $1/r^2$ dependency) could be expected to yield a fall in O/C of greater than 85% in treatment going from 15 to 80 mm. This shows that illumination of the sample occurs from a wide surface of the source, and the photonic flux is well collimated downstream.

4. Conclusions

The characteristics of a newly developed two-chamber low-pressure plasma reactor have been investigated in the low ion power modification of polystyrene. The source provides independent control of the charged particle concentration and ion energy (<25 eV) through a technique of electrical grid biasing. Ion power densities to the surface in the range 0.7 to 15.5 W m⁻² can be achieved, much lower than in conventional barrel reactors, where high fluxes and high ion bombarding energies (>50 eV) are typical. The results show that even at the highest ion power fluxes, surface treatment in the device is dominated by the photon (VUV) flux and generally, that ions may not have any significant role in the modification process for ion power densities below a certain threshold. Based on the results here, a lower limit to this threshold is about 16 W m⁻². Through the total elimination of the ionic flux, through grid biasing, and also the use of a transparent window to stop all charged and neutral particles, it has been shown that the main plasma does in fact acts as a very effective VUV source. There is good collimation of the photonic flux emerging from the main source downstream, which gives rise to short process times of a few minutes to achieve O/C ratios in the upper surface of 10%. This treatment time is an order of magnitude shorter than for other plasma based VUV sources described in the literature.

In future studies, we plan to re-design the discharge to facilitate controlled ion bombardment with elimination of the VUV flux and also increase the available ion powers to test the point at which point ions begin to play in the modification process.

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