

Epoxide-Functionalized Solid Surfaces

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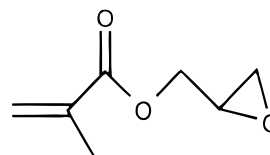
Reactive epoxide groups can be directly fixed onto solid surfaces by pulsed plasma polymerization of glycidyl methacrylate. These functionalized substrates are ideally suited for subsequent derivatization chemistries utilizing nucleophilic reagents, and also adhesion promotion.

1. Introduction

The surface functionalization of solid objects is a topic of considerable technological relevance, since it potentially offers a highly cost-effective means for improving substrate performance without affecting the overall bulk properties. For instance, surface epoxide groups can provide binding sites for nucleophilic reagents,¹ such as amines.^{2–7} Important applications include biotechnology^{6–9} and adhesion.^{2,10–13} Existing methods for incorporating epoxides onto solid surfaces involve UV^{4,5,8,11} or electron beam⁶ irradiation of a substrate followed by immersion into a solution containing an initiator and a polymerizable epoxide monomer (e.g., glycidyl methacrylate) leading to polymer growth at the surface. Other possibilities comprise plasma activation of a substrate followed by solution phase grafting of a polymerizable epoxide monomer,^{3,12} or alternatively the direct coupling of epoxysilanes onto silicon wafers.¹⁴ All of these approaches suffer drawbacks such as multistep

processes, solution-phase chemistry, and a tendency for being substrate-specific.

Plasma polymerization¹⁵ of monomers containing epoxide functionalities is one potential way of overcoming these limitations. In the past, plasma polymers have often been considered to be structurally dissimilar compared to their conventionally synthesized polymer counterparts, on the basis of high levels of cross-linking and lack of a regular repeat unit.¹⁵ These structural flaws can be attributed to the plasma environment, generating a wide variety of reactive intermediates. More recently, it has been found that pulsing the electric discharge on the millisecond to microsecond time scale can significantly improve structural retention of the parent monomer species,^{16,17} and in some cases conventional linear polymers have been produced.¹⁸ Under such experimental conditions, repetitive short bursts of plasma are understood to control the number and lifetime of active species created during the on-period. Conventional reaction pathways then proceed during the off-period (e.g., polymerization).¹⁹ In this article, the pulsed plasma polymerization of glycidyl methacrylate is described as a solventless method for functionalizing solid surfaces with epoxide groups. This is achieved by selective polymerization of the methacrylate carbon-carbon double bond while leaving the epoxide group intact.



Structure I: Glycidyl methacrylate

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2. Experimental Section

Plasma polymerization of glycidyl methacrylate (Aldrich, +97%, further purified using several freeze-pump-thaw cycles) was carried out in a cylindrical glass reactor pumped by a mechanical rotary pump via a liquid nitrogen cold trap (base pressure = 8×10^{-3} Torr, and leak rate = 3.2×10^{-9} mol s^{-1}). A copper coil wrapped around the reactor was coupled to a 13.56 MHz radio frequency power supply via an LC matching network. Prior to each experiment, the chamber was cleaned using a 50 W air plasma at 0.2 Torr. Glycidyl methacrylate monomer was then introduced via a fine control needle valve at a pressure of 0.2 Torr and 1.2×10^{-7} mol s^{-1} flow rate, followed by film deposition for 15 min. Upon completion, the reactor was purged with monomer for 5 min. In the case of pulsed plasma polymerization, a signal generator was used to trigger the RF supply, and the pulse shape was monitored with an oscilloscope.

Quartz crystal deposition rate measurements were carried out during plasma polymerization using a Varian 985-7013 thickness monitor.

The epoxide-functionalized surfaces were then reacted with trifluoroacetic acid vapor (Fluorochem Limited, +99.5%) for 30 min followed by evacuation to remove any absorbed remnants. Other nucleophilic derivatization reactions included exposure to ethylenediamine (Aldrich, +99%), and diethylamine (Sigma, +98%); here plasma polymer coated glass slides were immersed into a solution of the amine diluted with methanol (Fisher, +99.8%) for 24 h, and then rinsed in pure methanol.

X-ray photoelectron spectroscopy (XPS) analysis was performed using a Kratos ES300 spectrometer equipped with a Mg $K\alpha$ X-ray source and an hemispherical analyzer operating in fixed retard ratio mode (22:1). Photoelectrons were collected at a take-off angle of 30° from the substrate normal. The elemental composition was calculated using sensitivity factors derived from chemical standards, C(1s):O(1s):F(1s):N(1s) equals 1.00:0.57:0.67:0.74, respectively. All binding energies were referenced to the C(1s) hydrocarbon peak at 285.0 eV. A Marquardt minimization computer program was used to fit core level envelopes with fixed width Gaussian peak shapes.

Transmission infrared spectra of plasma polymer films deposited onto NaCl plates were acquired on a Mattson Polaris FTIR instrument at a resolution of 4 cm^{-1} and averaged over 100 scans.

TOF-SIMS analysis was carried out with a Physical Electronics 7200 instrument which has been described previously.²² The primary ion beam (8 keV Cs^+) with a spot size of $\sim 50 \mu\text{m}$ was rastered over an area of $100 \times 100 \mu\text{m}$ keeping the total dose well under 10^{13} ions cm^{-2} (static conditions).

For the adhesion measurements, a drop ($\sim 3 \mu\text{L}$) of coupling agent solution (ethylenediamine, 0.5 M in 1,4-dioxane (Aldrich, +99%)) was placed between two glycidyl methacrylate plasma polymer coated strips of polymer film (polyethylene, PE, ICI, 0.08 mm thickness, or polytetrafluoroethylene, PTFE, Goodfellow, 0.25 mm thickness), and then cured overnight at 60°C in an oven. Subsequently, single lap and T-peel adhesion tests^{20,21} were carried out using an Instron 5543 tensiometer operating at a crosshead speed of 1 mm min^{-1} .

3. Results and Discussion

a. Pulsed Plasma Polymerization. XPS analysis of the glycidyl methacrylate plasma polymer coatings confirmed the presence of only carbon and oxygen at the surface, with no Si(2p) signal from the underlying glass substrate showing through. The C(1s) envelope

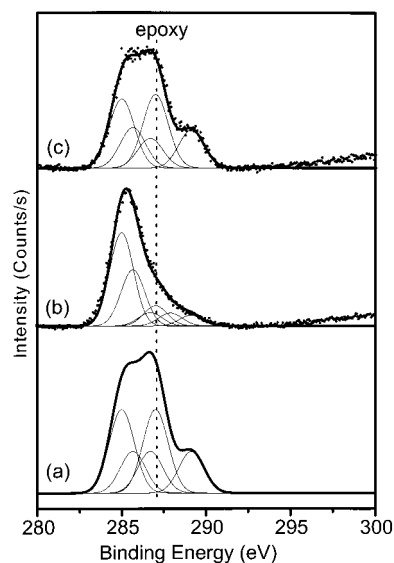


Figure 1. C(1s) XPS spectra of glycidyl methacrylate plasma polymers deposited onto a flat glass substrate: (a) theoretical curve, (b) 3 W continuous wave, and (c) pulsed (time on = 20 μs , time off = 20 ms, peak power = 40 W).

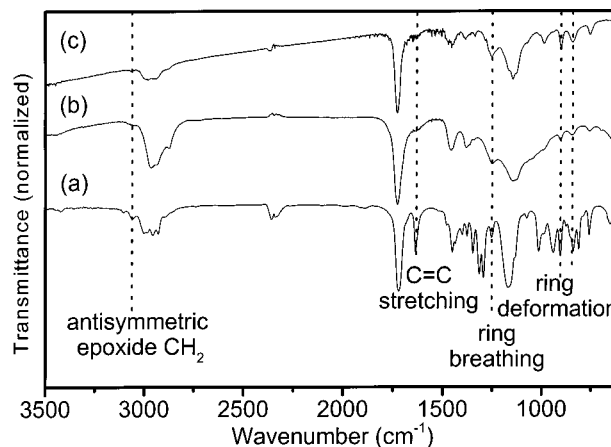


Figure 2. Infrared spectra of (a) glycidyl methacrylate monomer, (b) 3 W continuous wave plasma polymer, and (c) pulsed plasma polymer (time on = 20 μs , time off = 20 ms, peak power = 40 W).

Table 1. XPS Atomic Percentages for Glycidyl Methacrylate Plasma Polymers

conditions	elemental %		total carbon %	
	% C	% O	% Epoxide	% (C=O)O
continuous wave	77.5 ± 0.5	22.5 ± 0.5	7.1 ± 0.5	6.5 ± 0.5
pulsed	73 ± 1	27 ± 1	19.1 ± 0.5	10.6 ± 0.3
theoretical	70	30	20	10

contained a variety of carbon functionalities for both the continuous wave and pulsed plasma polymer layers: CH (285.0 eV), $\text{C}(\text{CH}_3)(\text{C}=\text{O})\text{O}$ (285.7 eV), $\text{O}-\text{CH}_2-\text{CO}$ (286.7 eV), epoxide carbons (287.2 eV), $\text{C}=\text{O}$ (287.8 eV), and $\text{C}(\text{=O})\text{O}$ (289.1 eV), Figure 1. Apart from the carbonyl group at 287.8 eV (associated with the continuous wave plasma polymer), the remaining peak assignments are referenced to XPS spectra obtained from conventional solution phase polymerized glycidyl methacrylate.²² Pulsed plasma polymerization yielded greater retention of epoxide groups in the deposited film compared to continuous wave conditions (Figure 1 and Table 1).

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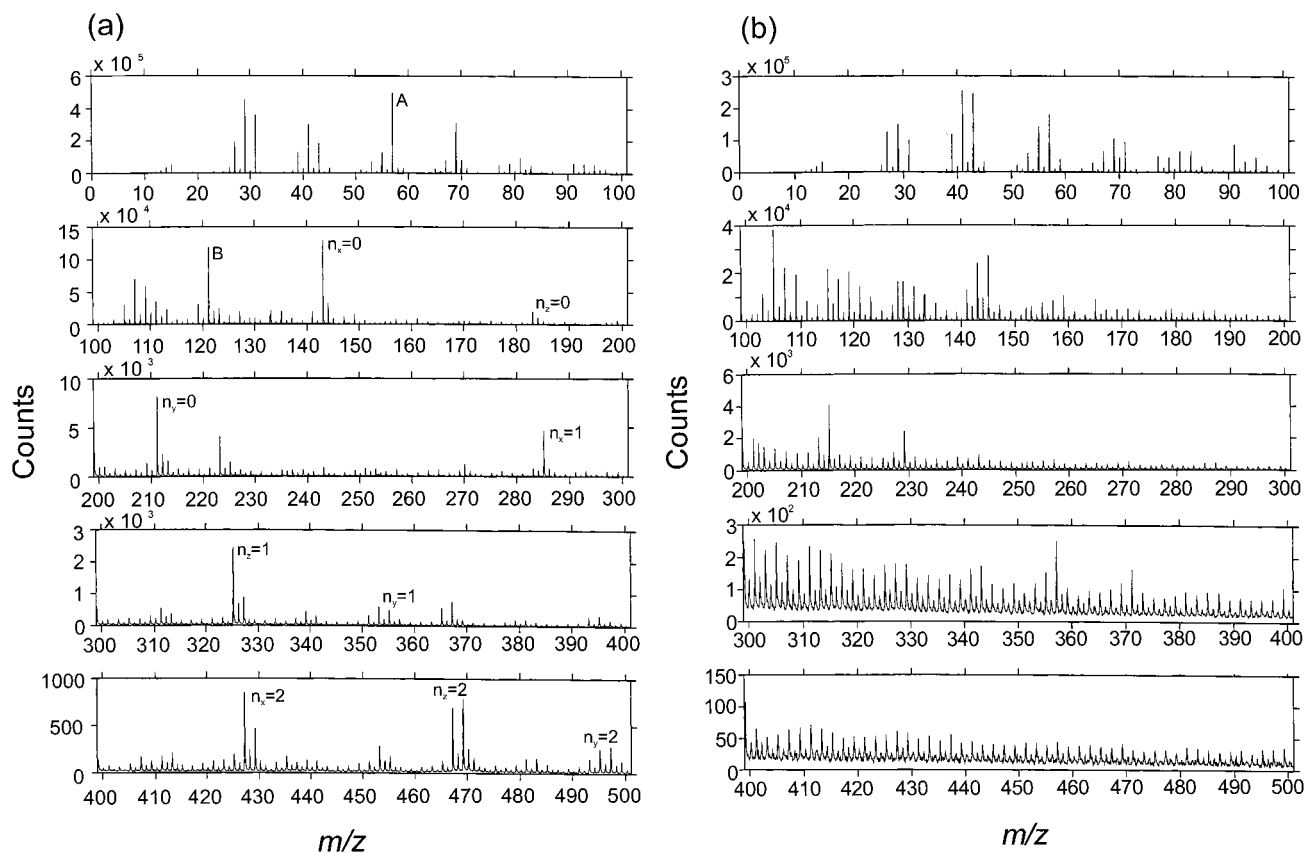


Figure 3. Positive ion TOF-SIMS spectra of (a) pulsed plasma polymer (time on = 20 μ s, time off = 20 ms, peak power = 40 W) and (b) 3 W continuous wave plasma polymer.

Infrared spectroscopy was used to probe the molecular structure of the plasma polymer coatings (Figure 2). For the glycidyl methacrylate monomer, the following band assignments were made: epoxide ring C-H stretching (3063 cm^{-1}), C-H stretching (3000–2900 cm^{-1}), acrylate carbonyl stretching (1720 cm^{-1}), acrylate C=C stretching (1637 cm^{-1}), epoxide ring breathing (1253 cm^{-1}), antisymmetric epoxide ring deformation (908 cm^{-1}), and symmetric epoxide ring deformation (842 cm^{-1}).^{1,23} The weak absorption feature present at 2360 cm^{-1} can be attributed to background CO_2 present in the FTIR spectrometer. Continuous wave plasma deposition of glycidyl methacrylate gave rise to broad infrared absorption features: epoxide ring C-H stretching (3060 cm^{-1}), C-H stretching (3000–2900 cm^{-1}), saturated ester C=O stretching (1728 cm^{-1}), C=C stretching (1630 cm^{-1}), epoxide ring breathing (1253 cm^{-1}), antisymmetric epoxide ring deformation (908 cm^{-1}), and symmetric epoxide ring deformation (842 cm^{-1}). The epoxide ring and carbon-carbon double bond features were much weaker compared to the monomer, whereas the C-H stretching region was more intense. All the bands associated with the glycidyl methacrylate monomer were clearly discernible following pulsed plasma polymerization, except for the methacrylate carbon-carbon double-bond feature which had disappeared during polymerization. The more intense infrared absorption bands belonging to the epoxide ring confirmed that greater structural retention had occurred during electrical pulsing conditions (despite the film being thinner—see deposition rate measurements below).

Comparison of the positive ion TOF-SIMS spectra for continuous wave and pulsed plasma polymer layers

confirmed the greater structural integrity of the latter, Figure 3 and Table 2. For continuous wave plasma polymerization, a large range of masses are observed, which can be taken as being indicative of extensive monomer fragmentation and rearrangement during plasma deposition. In contrast, the pulsed plasma counterpart displays well-defined polymer repeat units which have been assigned on the basis of the positive ion SIMS spectra obtained for conventionally polymerized methyl methacrylate.²⁴

Quartz crystal deposition rate measurements provided values of $(19 \pm 3) \times 10^{-9}$ and $(2.5 \pm 0.5) \times 10^{-9}$ $\text{g s}^{-1} \text{cm}^{-2}$ for the continuous wave and pulsed conditions, respectively. The lower value obtained for pulsed plasma polymerization can be mainly attributed to less energy input. In fact the deposition efficiency²⁵ (expressed as deposition rate divided by power) was calculated to be 6.3 and 63×10^{-9} $\text{g cm}^{-2} \text{J}^{-1}$ respectively. This implies that there is greater deposition per quantity of input energy in the case of pulsed plasma polymerization.

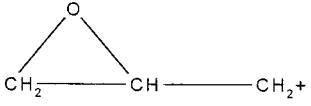
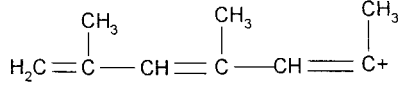
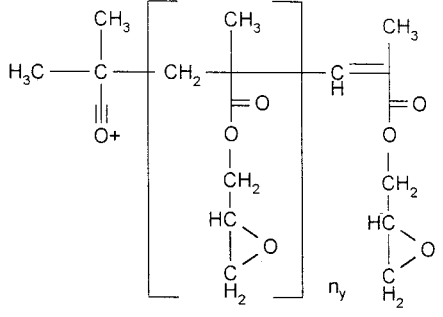
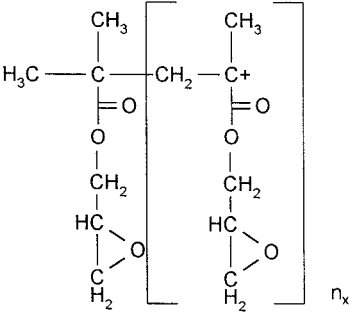
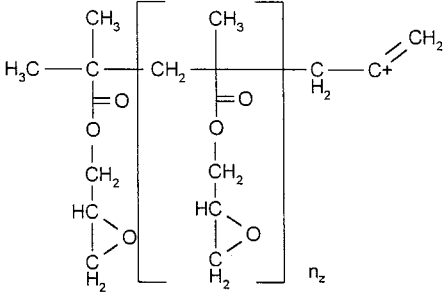
b. Reactivity of Epoxide Groups. Epoxide-functionalized surfaces were derivatized with a variety of nucleophilic reagents (e.g., carboxylic acids and amines). Typically, reaction occurs at the electrophilic epoxide carbon centers leading to ring opening.¹ In the case of

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Table 2. Positive Ion TOF-SIMS Assignments of Glycidyl Methacrylate Plasma Polymers

 <p>A $m/z = 57$</p>	 <p>B $m/z = 121$</p>																													
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n_x	0	1	2	3	4	5																								
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Scheme 1. Reaction between an Epoxide Ring and a Nucleophilic Reagent



carboxylic acids and amines, attack on the less substituted epoxide carbon is normally favored to yield the secondary alcohol, Scheme 1.²⁶

Trifluoroacetic acid vapor underwent reaction to a greater extent with the pulsed plasma polymer film (XPS measured $4.1 \pm 0.5\%$ and $16.0 \pm 0.8\%$ fluorine for the continuous and pulsed plasma polymer coatings respectively), Scheme 2. This enhancement in reactivity for the pulsed plasma polymer layer was confirmed by the identification of CF_3 functionalities at 293.3 eV in the C(1s) envelope,²² Figure 4. The proportion of epoxide groups which had undergone monoesterification was calculated using the F(1s) peak area as follows:^{27,28}

$$\%[\text{F}] = \frac{3/2x[\text{epoxide}]_0}{[\text{C}]_0 + [\text{O}]_0 + 7/2x[\text{epoxide}]_0} \times 100 \quad (1)$$

where x is the fraction of reacted epoxides, $[\text{epoxide}]_0$ is the initial concentration of carbon atoms belonging to epoxide groups (as determined from the C(1s) envelope, Table 1), $[\text{C}]_0$ is the concentration of carbon prior to

reaction, $[\text{O}]_0$ is the concentration of oxygen prior to reaction, and $\%[\text{F}]$ is the percentage of fluorine detected at the surface. On this basis, 42% and 89% of the surface epoxide groups were calculated to have undergone reaction for the continuous wave and pulsed plasma polymer layers, respectively. Therefore, it appears that the proportion of epoxide group centers calculated from the C(1s) peak fitting (Figure 1 and Table 1) for continuous wave conditions is probably an overestimation. Other groups such as ethers or carbonyls must also be present in the plasma polymer layer contributing to the assigned epoxide component at around 287.2 eV in the C(1s) spectrum. Alternatively, greater cross-linking may hinder reaction throughout the whole XPS sampling depth. Excess trifluoroacetic acid could potentially react further with alcohol groups formed during epoxide ring opening to produce a diester and this may be contributing to a slight overestimation in the overall reaction yield.¹

Diethylamine was used to assess the reactivity of surface epoxide groups toward amines. This secondary amine was chosen because it is capable of reacting only

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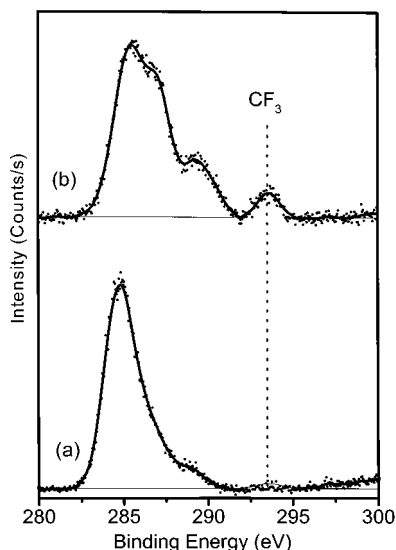
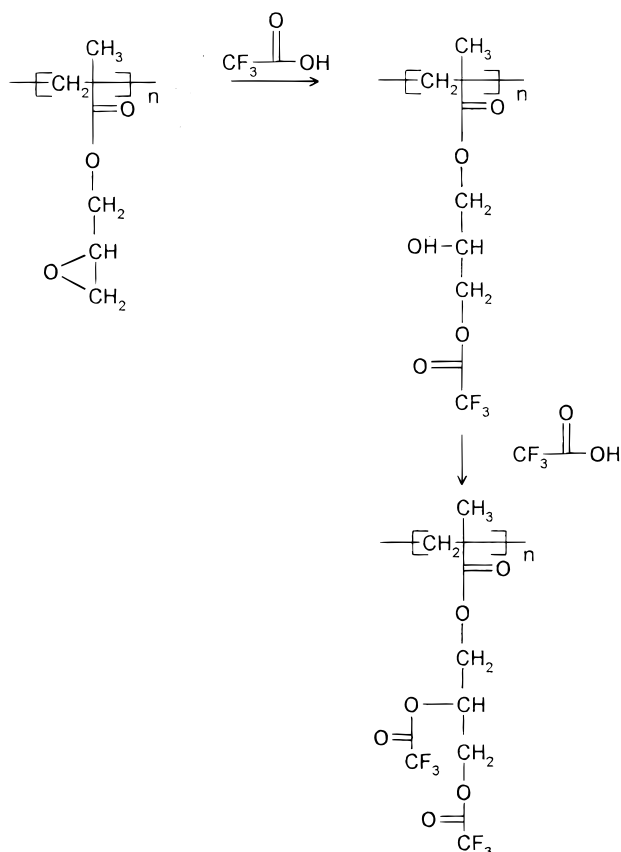


Figure 4. C(1s) XPS spectra of plasma polymers exposed to trifluoroacetic acid vapor: (a) 3 W continuous wave and (b) pulsed (time on = 20 μ s, time off = 20 ms, peak power = 40 W).

Scheme 2. Reaction of Poly(glycidyl methacrylate) with Trifluoroacetic Acid



once with an epoxide center¹ (Scheme 2) therefore making it much easier to calculate the number of aminated epoxides from the corresponding N(1s) peak area:

$$\%[\text{N}] = \frac{1/2x[\text{epoxide}]_0}{[\text{C}]_0 + [\text{O}]_0 + 5/2x[\text{epoxide}]_0} \cdot 100 \quad (2)$$

On this basis, the 4.4% nitrogen detected by XPS for the pulsed plasma polymer layer corresponds to 59% of

Scheme 3. Reaction of Poly(glycidyl methacrylate) with Diethylamine

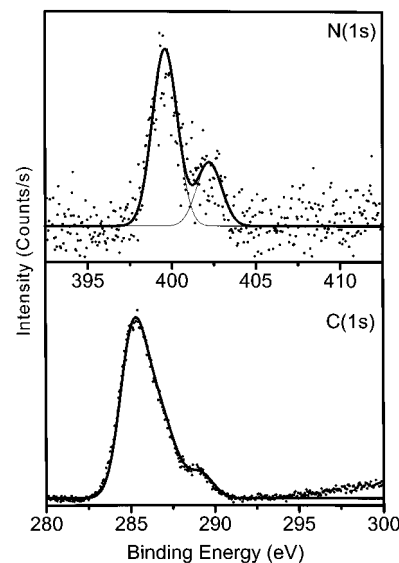
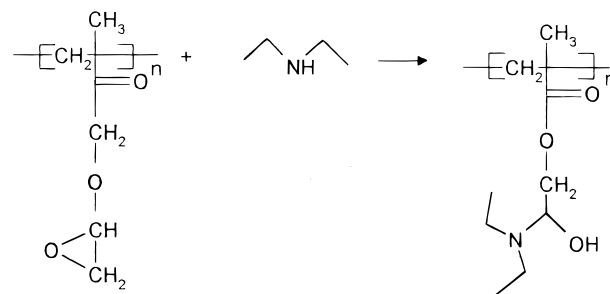


Figure 5. N(1s) and C(1s) XPS spectra of glycidyl methacrylate pulsed plasma polymer derivatized with diethylamine (time on = 20 μ s, time off = 20 ms, peak power = 40 W).

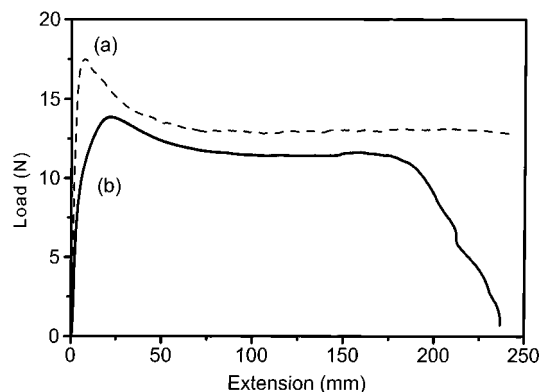


Figure 6. Stress/strain curves of (a) polyethylene substrate and (b) 1 cm² single lap joint of pulsed glycidyl methacrylate plasma polymer coated polyethylene strips (time on = 20 μ s, time off = 20 ms, peak power = 40 W).

the surface epoxide groups having undergone reaction as depicted in Scheme 3. The major peak seen in the N(1s) spectra at 399.8 eV can be assigned to a neutral nitrogen environment, while the small feature at 402.1 eV is due to positively charged nitrogen (Figure 5). The latter can be attributed to protonation by atmospheric moisture,²⁹ rather than the reaction of the amine center with an adjacent epoxide group.

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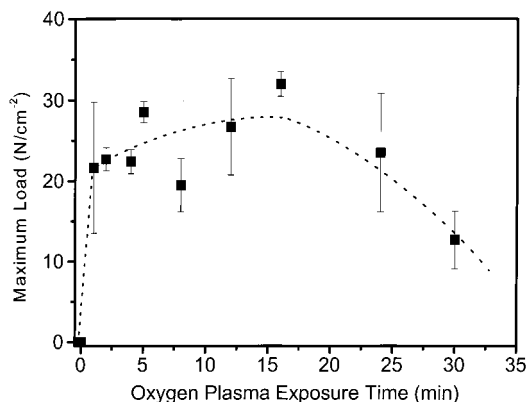


Figure 7. Influence of 20 W oxygen plasma pretreatment time upon lap joint strength for PTFE substrates which were subsequently coated with pulsed glycidyl methacrylate plasma polymer (time on = 20 μ s, time off = 20 ms, peak power = 40 W).

c. Adhesion. The reaction between surface epoxide groups and amines was further investigated using ethylenediamine ($\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$) as a coupling agent for adhesion. A drop of 0.5 M solution of ethylenediamine dissolved in 1,4-dioxane was placed between two pieces of plasma polymer coated polyethylene. The samples were then annealed overnight at 60 $^\circ\text{C}$ to allow solvent evaporation and bonding.¹³ In the case of pulsed plasma polymer layers, single lap joint and T-peel adhesion measurements indicated that the adhesive bond strength was greater than the threshold for failure of the host polyethylene matrix (this was evident from the failure not occurring in the region of the joint, but adjacent to it) (Figure 6), whereas the actual joint was found to fail for continuous wave plasma polymerization.

No adhesion between polyethylene strips was observed in the absence of either the plasma polymer or the coupling agent.

O_2 plasma roughening^{30,31} of the PTFE substrate was necessary prior to pulsed plasma deposition of glycidyl methacrylate in order to achieve good adhesion. Here the joint eventually failed rather than the substrate, since PTFE was much stronger than PE (bulk failure of PTFE occurred at 45 N). The duration of oxygen plasma pretreatment was found to affect the strength of the adhesive joint (Figure 7). Excessively long oxygen plasma exposures were probably leading to polymer chain scission and the formation of low molecular weight material, which is known to have a detrimental effect upon adhesion.

4. Conclusions

Pulsed plasma polymerization of glycidyl methacrylate is a simple one-step method for functionalizing solid substrates with epoxide groups. These surfaces are amenable to conventional epoxide derivatization chemistries. In addition they have been found to offer excellent adhesion performance.

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