Chemical surface preparation for metallization of stereolithography polymers

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Abstract

Chemical surface preparation specifically for stereolithography (SLA) polymers prior to its metallization is reported for the first time in the present paper. Contact angle analysis was conducted to assess the surface hydrophilicity so as to optimize the preparation process. The applicability of this technology was verified by subsequent metallization process. This introduces an efficient method for metallization of SLA polymers and enhances its performance in applications. X-ray diffraction (XRD) and atomic force microscopy (AFM) image analysis were applied to understand the phase composition and the micromorphologies of the substrate. Surface profiling and optical microscopy were applied for surface analysis to understand the progression of surface modification during chemical preparation process. Crown copyright © 2000 Published by Elsevier Science B.V. All rights reserved.

Keywords: Etching; Polymer; Stereolithography

1. Introduction

Stereolithography (SLA) is a new technology linking the power of computer graphics to the rapid formation of a solid, shaped object [1,2]. This technology uses UV laser to selectively solidify successive thin layers of a photocurable resin and provides great economies for both the design laboratory and the modeling process [1,3]. Since Hull’s invention of SLA in 1984, this novel technology has enabled a new method for rapid prototyping (RP), which appeared in 1988, that allows designers to verify their product design at an early stage, by using 3D representations for design review with sales, marketing and production engineers [4–6]. However, many of these systems produce only fragile parts, which can only be used for form-and-fit analysis but cannot be tested in an apparatus as though they were functional parts.

Since 1995, Yeung and McKeen [7], McKeen and Yeung [8] and Yeung et al. [9] have developed a novel technology to deposit metals onto the surfaces of non-metallic RP parts. Of all the available metallization processes such as electroless plating, physical vapor deposition (PVD) and chemical vapor deposition (CVD), the former is the most applicable for SLA parts due to its possession of combined characteristics such as uniformity, simple operation, low cost and no damage to the substrate.
In order to apply electroless plating to a non-catalytic surface, the surface must be subjected to a series of pretreatment such as pickling, sensitization and activation. Of all the three pretreatment processes, pickling is an essential process which provides the substrate with cavities, and in some cases, a modified chemistry which improves the wettability of the surface and sometimes renders a hydrophobic surface hydrophilic. Chemical etching is a commonly known pickling process that has been successfully applied to numerous types of polymers such as ABS [10]. Using the same approach, the present communication introduces a chemical etching process specific for pickling of polymers fabricated by laser-induced polymerization using SLA apparatus.

2. Experimental

2.1. Sample fabrication

Simple SLA RP samples of 30 mm × 30 mm × 10 mm were fabricated in house. SLA5195 resin provided by Ciba Geigy was used for fabrication. It is of note that the resin is widely used in RP but the chemical composition of the final polymer is unknown to customers due to the commercial concerns. There are three types of commercially available SLA polymers which are coded as SLA5170, SLA5180 and SLA5195. The only information revealed by Ciba Geigy about the SLA5195 resin, used in our current research, is that it is a complicated six-component mixture containing cycloaliphatic epoxy resin, aliphatic glycidyl ether, polyols, modified acrylate ester, acrylate ester and photocuring agent. The parts were designed on a Proengineer with Version 18.0 software provided by Parametric Technologies. Care was taken to place the resin, as supplied, in the vat of Model SLA5000 SLA apparatus where the resin is photopolymerized during a laser-induced photocuring process and parts characterized of layered structure are manufactured. The system is supplied by 3D Systems, equipped with Build-Station Version 4.1 software. The parts produced are then drained and subsequently rinsed in a RAMCO tank containing TPM solvent with mechanical agitation, and subsequently thoroughly rinsed with water to remove liquid resin, if it still remains, from the surface of the SLA parts. The cleaned parts are then subjected to a 4-h post-curing process in a UV irradiation chamber, an attachment of the 3D SLA5000, to complete the entire photocuring process.

2.2. Chemical etching

Chemicals, CrO₃ and H₂SO₄, of AR grade used for chemical etching of the parts were purchased from Sigma. It can be reasonably expected that factors such as bath composition, temperature and the duration of the etching process may affect the etching process and hence, the finishing of the substrate surface. Taguchi design, a simple and fast mathematical method to study the effects of various factors, was applied in the present research. Temperature was controlled using NESLAB GP200 water bath.

2.3. Contact angle analysis

As is known, there exists an intimate link between contact angle and wettability or hydrophilicity [11]. To assess the hydrophilicity of the surfaces subjected to different etching so as to optimize the operation conditions, contact angle was measured using a Rame-Hart Model 100 Contact Angle Goniometer equipped with a microsyringe attachment. Deionized, 18-MΩ water, which had been filtered to remove hydrocarbons, was employed as the probe liquid. Four measurements were made on each sample, and the data are presented as a mean with a standard deviation.

2.4. Physical analysis

X-ray photoelectron spectroscopy (XPS) was applied to understand more about the composition and chemistry of the SLA5195 part fabricated. Model SSX-100 XPS machine was manufactured by Surface Science Laboratories.

Phase compositional analysis of the sample was carried out using Philips X’PERT-MRD. Cu LFF X-ray tube was employed for measurements. Model Topometrix Explorer Atomic Force Microscopy
AFM provided by Topometrix was used for topographic image analysis. Morphological analysis was conducted on the surfaces before and after etching, using Model Olympus PMG3 optical microscope. Surface roughness and profile were analyzed using Model WYCO NT2000 Surface Profiler.

3. Results and discussion

3.1. XPS analysis

As was aforementioned, information provided by Ciba Geigy revealed that the SLA5195 resin is a complicated six-component mixture containing cycloaliphatic epoxy resin, aliphatic glycidyl ether, polyols, modified acrylate ester, acrylate ester and photocuring agent. To further understand the chemistry of the polymer formed by laser-induced polymerization, survey scans for elemental composition were taken and the spectrum is presented in Fig. 1.

As is manifested in Fig. 1, there exist two peaks at the binding energies of 285 and 530 eV regions, corresponding to the 1S of C and O, respectively. The elemental composition of the sample is calculated as 78.7% carbon and 21.3% oxygen. It ought to be mentioned that H is not detectable by XPS. To further understand the nature of bonding, survey scans for higher-resolution carbon spectra were taken of the cured polymer and the spectra are presented in Fig. 2. The high-resolution carbon spectra provide information about the oxidation state of the carbon at the surface of the polymer. Typically, the largest peak is attributable to the C–C and C–H bonds and is assigned a binding energy of 281.75 eV. The peak from carbon in a higher oxidation state is shifted to a higher binding energy so that the peaks from carbon singly bonded to oxygen are shifted to 1.06 and 1.87 eV. The co-existence of two C–O bonds is attributed to the environmental difference of singly bonded carbon such as formations of H–C=O and O–C=O. Similarly, the peak from carbon double bond, C=O, is shifted 3.63 eV and the peak attributable to O=C=O is shifted to 4.16 eV. The above results revealed that carbon in the SLA5195 polymer has different energy states when bonded to oxygen, namely, different binding energy. This indicates a non-uniform surface energy state of the SLA5195 polymer and therefore, a possible non-uniform phase structure formed during polymerization process.

Fig. 1. The XPS spectrum of SLA5195 polymer showing the elemental composition.
3.2. Chemical etching

Chemical etching was carried out in an aqueous solution containing \( \text{CrO}_3 \) and \( \text{H}_2\text{SO}_4 \) and deionized water, following the Taguchi orthogonal array (see Table 1). The Taguchi array consists of four factors, which are temperature, duration of etching and \( \text{CrO}_3 \) and \( \text{H}_2\text{SO}_4 \) concentrations. Three levels were assigned to each factor. The solution was kept stirred and \( \text{CrO}_3 \) and \( \text{H}_2\text{SO}_4 \) were added slowly during the entire dissolution process. Furthermore, due to its exothermic nature of dissolution, the solution made was cooled down to below each nominated temperature in Table 1 and was then heated up to and maintained at the nominated temperature using NESLAB GP200 water bath. In addition, as the practical etching process was also noticed of exothermic, agitation of the solution was necessary to ensure a homogeneous temperature distribution. Temperature was monitored during the entire etching process and a fluctuation of \( \pm 2^\circ\text{C} \) was observed. The etched samples were then thoroughly rinsed with distilled water for subsequent analysis.

3.3. Contact angle analysis

As was aforementioned, the objective of chemical etching was to improve the hydrophilicity of the surface. The effects of chemical etching were therefore assessed by contact angle measurements, shown in Table 2.

The data are presented in Table 2 as static, advancing and receding contact angles. The static angle was determined by applying approximately 0.004 ml of water on the surface and measuring the angle that the static drop makes with the surface. The advancing angle is measured as water is added to the drop and the front advances. The receding angle is measured as water is removed from the drop and the front recedes. As shown in Table 2, the static and advancing contact angles give identical hydrophilic-

![Fig. 2. High-resolution carbon spectra of SLA5195 polymer showing different energy state of carbon.](image)

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Temperature (°C)</th>
<th>Etching (min)</th>
<th>( \text{CrO}_3 ) (g/l)</th>
<th>( \text{H}_2\text{SO}_4 ) (g/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>25</td>
<td>10</td>
<td>300</td>
<td>0</td>
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<td>2</td>
<td>25</td>
<td>30</td>
<td>600</td>
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<td>3</td>
<td>25</td>
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<td>150</td>
</tr>
<tr>
<td>5</td>
<td>50</td>
<td>30</td>
<td>900</td>
<td>0</td>
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<td>60</td>
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<td>8</td>
<td>75</td>
<td>30</td>
<td>300</td>
<td>150</td>
</tr>
<tr>
<td>9</td>
<td>75</td>
<td>60</td>
<td>600</td>
<td>0</td>
</tr>
<tr>
<td>10</td>
<td>Sample not subjected to chemical etching</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 1

Taguchi orthogonal arrays \([L9(3^4)]\) for chemical etching
Table 2
Contact angles of surfaces subjected to different chemical etching

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Static angle (°)</th>
<th>Advancing angle (°)</th>
<th>Receding angle (°)</th>
<th>Comments on surface</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>72.9</td>
<td>79.3</td>
<td>31.0</td>
<td>shiny, heterogeneous</td>
</tr>
<tr>
<td>2</td>
<td>45.5</td>
<td>51.9</td>
<td>13.0</td>
<td>homogenous</td>
</tr>
<tr>
<td>3</td>
<td>40.7</td>
<td>43.7</td>
<td>10.7</td>
<td>homogenous</td>
</tr>
<tr>
<td>4</td>
<td>38.2</td>
<td>43.0</td>
<td>13.0</td>
<td>homogenous</td>
</tr>
<tr>
<td>5</td>
<td>45.9</td>
<td>50.8</td>
<td>14.0</td>
<td>shiny, crazed</td>
</tr>
<tr>
<td>6</td>
<td>59.8</td>
<td>66.3</td>
<td>14.5</td>
<td>heterogeneous, crazed</td>
</tr>
<tr>
<td>7</td>
<td>52.4</td>
<td>58.5</td>
<td>15.9</td>
<td>shiny, crazed</td>
</tr>
<tr>
<td>8</td>
<td>65.9</td>
<td>71.9</td>
<td>&lt; 10</td>
<td>heterogeneous, crazed</td>
</tr>
<tr>
<td>9</td>
<td>62.0</td>
<td>66.6</td>
<td>13.8</td>
<td>heterogeneous, crazed</td>
</tr>
<tr>
<td>10</td>
<td>72.8</td>
<td>78.5</td>
<td>27.9</td>
<td>unetched homogenous sample</td>
</tr>
</tbody>
</table>

ity trends. The receding contact angles give very similar, low results for all samples, except the unetched sample, no. 10, and the inadequately etched sample, no. 1, which are higher. Sample no. 8 is anomalous, because it has relatively high static and advancing contact angles and the lowest receding contact angle. This is probably attributable to the heterogeneity of the surface. From the results, we can see that, the unetched sample (no. 10) and the sample (no. 1), which was subjected to an apparent insufficient etching, exhibit the highest contact angles, namely, the lowest hydrophilicity. The rest of the samples subjected to different degrees of chemical etching show a decrease in contact angle. This
clearly indicates a significant improvement of the surface hydrophilicity by chemical etching. The effect of chemical etching varies according to the variation of operation conditions such as composition of the oxidizing reagents, temperature and duration of etching. The best operation condition yields a drastic decrease of static contact angle from 72.8° to 38.2°, corresponding to the unetched sample and the chemically etched sample, respectively. It is readily apparent in Table 2 that chemical etching provides, in a wide operation range, a hydrophilic surface for metallization.

In addition, it ought to be mentioned that the above contact angle data were not obtained from ideally smooth surfaces and are therefore not equilibrium contact angles. The equilibrium contact angle $\theta_e$ corresponds to the lowest energy state for a system. On an ideally smooth and compositionally homogeneous surface, the equilibrium contact angle is the Young’s angle $\theta_y$. However, many real surfaces are rough or heterogeneous. A liquid drop resting on such a surface may reside in a metastable equilibrium (energy trough separated from neighboring states by energy barriers), exhibiting a metastable contact angle. In this case, advancing and receding angles are different, known as hysteresis. The difference, $\theta_a - \theta_r$, is the extent of hysteresis. The general Young equation is then invalid for contact angle analysis on a rough surface. Numerous works have been done to deal with contact angle measurements on a rough surface and the first model was proposed by Wenzel [12]. Joanny and De Gennes [13] also proposed a model analyzing the surface roughness effect on the contact angle measurements. However, due to the fact that contact angle measurements are performed on surfaces of different roughness, practical contact angle analysis is normally based on experimental practices. It is generally accepted that hysteresis will be negligible when the surface roughness is below 0.5 μm [14,15]. Surface profiling studies revealed that the average microroughness of our samples ranged from 0.31 (X profiling) to 0.43 μm (Y profiling), which are within the negligible topographic limit. However, contact angle for each sample was still measured at four different locations on the surface, and measurement at each location was repeated for three times.

3.4. Optical microscopy and surface profiling studies

In order to understand the significant improvement on the hydrophilicity of the substrate surface.
during chemical etching, optical microscopy studies were performed. The unetched surface is shown in Fig. 3, observed at a magnification of 500 ×. It was observed that the unetched surface was not only very
smooth but also highly transparent, which made the optical microscope observation at lower magnification very difficult. In fact, good focusing was not accessible. A typical etched surface is presented in Fig. 4, showing a regularly distributed patterned feature. It is manifested that the surface is roughened during chemical etching process. Electroless nickel plating was subsequently carried out successfully on a chemically etched surface in a conventional bath but the unetched polymer surface was not platable at all. These verified the applicability of the present chemical etching process. The reason for this improvement may be attributable to the improved surface hydrophilicity and therefore, a better adhesion of the coating to the polymer surface. However, the possibility of a modified surface chemistry should not be excluded. These then lead to a conventional debate between two theories on the nature of adhesion that have been co-existing for many years. The first theory was ‘chemical bonding theory’ proposed based on the belief that there exists a chemical bonding between the coated metal and the plastic substrate [10]. The other theory is called ‘mechanical anchoring theory’ proposed based on the belief that a better adhesion of coating on a microroughened surface is due to the availability of microcavities which provide metal atoms better ‘anchoring sites’ [16]. This was supported by another interesting study conducted by Ebneth and Klimaschewski [17]. In their experiments on determining whether or not chemical bonding is a contributory factor to the adhesion, Ebneth and Klimaschewski plated different metals such as gold, silver and copper. Should chemical bond between metal and plastic be an essential contributory factor for adhesion, it would be influenced by the type of conductive metal deposited. This, however, was not the case shown by his experimental results. It is now generally believed that the microroughness of the plastic surface dominates the adhesion of coating but possible contribution of chemical bonding has never been excluded. To quantitatively analyze the roughness change before and after chemical etching, surface-profiling technique was applied. The 3D plots corresponding to samples without and with chemical etching are given in Figs. 5 and 6, respectively. It ought to be mentioned that the two figures are not of the same axis scales, which are automatically determined by the software. The measurements reveal that although the waviness (macroroughness, described by \( R_m \)) of the samples are almost identical, the microroughness, \( R_t \), of the chemically etched sample surface is significantly increased. This verifies the optical microscopic observation of the surface roughness change, which may contribute to the hydrophilicity of the surface.

It is readily apparent that microroughening of the surface is well-indicative of a selective chemical etching on the surface of the SLA part. To further understand the nature of this selective chemical etching process, a sample was overetched until the surface was severely crazed (see Fig. 7). As manifested, the etched surface shows four different features: plain surface (background), a grey strip area and two dark bands along both sides of the grey strip and spherical holes which may be the onset of the strip formation. Detailed observations were subsequently carefully conducted at a higher magnification (500 ×) for further understanding of the surface.
features. It was then found that different features did not come in focus simultaneously, indicating that these features are of different heights or depths. The sequence of focusing revealed that the plain area is the top surface and the grey strip is a ridge at a lower level and the two dark bands are of etched-in slots at the lowest level along both sides of the ridge. The images obtained at the same spot are given in Figs. 8–10, with focusing sequence from top of the surface, top of the ridge and the bottom of the slots. The dial-meter readings showed that the slots are of about 8 μm in depth and the ridge is about 5 μm in height as from the bottom of the slots. It ought to be mentioned that the outer patterned lines, known as ‘Newton’s Fringes’, generated from the interference of light at very thin edges between adjacent features are not characterized by the intrinsic feature of the surface. The abovementioned observations were confirmed by further surface profiling studies, shown in Fig. 11. The depth of the slots and the height of the ridge are very close to those measured by optical microscopy dial-meter. Fig. 12 provides a schematic of the above observations in favor of an easier understanding of the features of the chemically etched SLA5195 surface.

The aforementioned optical microscopy and surface profiling studies clearly suggested that the SLA5195 part is not a single-phase material, which prompted our XRD phase studies presented below.

3.5. X-ray diffraction (XRD) and AFM

The XRD measurements were conducted on a fresh SLA5195 sample. The diffraction pattern is presented in Fig. 13, showing two broad peaks at 2θ of 18.30° and 41.63°. As is known, the most dramatic difference among crystalline and amorphous materials is on how they scatter an X-ray beam [18,19]. The curve of scattered intensity vs. 2θ for a crystalline solid is almost zero everywhere except at
Fig. 11. The 2D surface profiling of the crazed polymer surface.

certain angles where high sharp maxima occur, corresponding to diffracted beams from grains of different orientation. On the contrary, a ‘perfect amorphous’ solid should yield no diffraction maxima due to the diffused X-ray scattering from randomly packed atoms in the atomic arrangement. However, materials practically referred to as ‘amorphous’ have structures characterized by an almost complete lack of periodicity and a tendency to ‘order’ only in the sense that the atoms are fairly tightly packed together and show a statistical preference for a particular inter-atomic distances. The diffraction result is an

Fig. 12. Schematic of a chemically etched trench.
X-ray scattering curve showing nothing more than one or two broad maxima \cite{19}. This is consistent with the XRD spectroscopy shown in Fig. 13, suggesting the existence of amorphous phase and/or amorphous-related phase in the SLA5195 sample. However, it ought to be mentioned the intensity of X-ray scattering peak at 18.30° is much greater than that of at 41.63°, indicating a certain degree of ‘ordered’ structure, namely, crystallinity. To verify this point, AFM imaging was subsequently conducted and is presented in Fig. 14. The shaded topographic image shows the presence of two different structures in the SLA5195 sample within a 5-μm square region. In the region on the right-hand side of the topographic image, the polymer shows a typical amorphous structure without ordering while the left-hand side of the image shows ordered and isolated fine grains of about 200 nm in diameter. This clearly revealed the co-existence of two phases in the SLA5195 polymer: an amorphous phase and a crystal phase. The small grain size is indicative of a fast solidification process during laser-induced curing process. However, difficulty arises in understanding the nature of this phase, for the peak is apparently too broad for single crystal and, on the other hand, the co-existence of other peaks should present if this is a polycrystalline phase, and this is apparently not the case shown by the XRD pattern. The laser-induced polymerization process for fabrication of the SLA material is then described below to understand this phenomenon. When an SLA part is made, laser beam scans over the liquid resin mixture at a high rate of about 5000 mm/s to form an instantly solidified thin layer of about 100 μm in thickness. Laser beam is then applied to form another layer on top of the previous layer. The direction of solidification is
always perpendicular to the direction of laser scanning. Liquid solidifies at a high rate from the top into the bulk of each layer and is repeated for every layer. This fast and oriented solidification process then yields a preferred orientation of crystallization during which very small grains are formed. It is now clarified that our SLA5195 polymer fabricated using laser-curing technique consists of amorphous and polycrystalline phases with preferred orientation. Based on the above discussion, the progression of chemical etching may be proposed below. This proposal adopts the models used for metal corrosion since chemical etching of materials, organic or inorganic, is essentially a corrosion process. The co-existence of two phases inevitably yields the existence of non-homogeneous phase boundaries, which are generally believed to have low 'corrosion' resistance. When the SLA part is immersed in the highly oxidizing media, localized etching therefore preferably starts and develops along the phase boundaries. In comparison to the phase boundary regions, the polycrystalline phase and the amorphous phase are homogeneous in nature with less defects, hence, suffer etching of a less degree. However, experimental results shown in Figs. 8–11 suggested that the grain boundaries in the polycrystalline phase may still lead to a preferred intergranular etching, which renders the polycrystalline phase a relatively lower etching rate than the amorphous phase in which no grain boundary is present. A schematic is given to illustrate the progression of chemical etching at different areas of the surface phase structure, presented in Fig. 15.

4. Conclusions

- Chemical etching was proved capable of significantly improving the hydrophilicity of the surface of SLA parts, which is beneficial for the subsequent pretreatment for metallization. The performance of metallization for RP is enhanced due to the uniformity of chemical etching.
The SLA part fabricated from laser-curing technique was found consisting of two phases: an amorphous phase and a polycrystalline phase with preferred orientation due to oriented laser-induced solidification during photopolymerization process.

The improvement to the surface hydrophilicity may be related to the creation and formation of grooved microtrenches on the surface due to the phase composition and structure of the SLA part. This, however, does not exclude the possibility of a modified surface chemistry. Further research is currently being conducted.

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References