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ADHESIVE BONDING OF ION BEAM TEXTURED METALS AND FLUOROPOLYMERS

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ABSTRACT

An electron bombardment argon ion source was used to ion etch various metals and fluoropolymers. The metal and fluoropolymers were exposed to (0.5 to 1.0) keV Ar ions at ion current densities of (0.2 to 1.5) mA/cm^2 for various exposure times. The resulting surface texture is in the form of needles or spires whose vertical dimensions may range from tenths to hundreds of micrometers, depending on the selection of beam energy, ion current density, and etch time. The bonding of textured surfaces is accomplished by ion beam texturing mating pieces of either metals or fluoropolymers and applying a bonding agent which wets in and around the microscopic cone-like structures. After bonding, both tensile and shear strength measurements were made on the samples. Also tested, for comparison's sake, were untextured and chemically etched fluoropolymers. The results of these measurements are presented in this paper.

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INTRODUCTION

Many methods have been studied to improve the strength of adhesive bonds to fluoropolymers. Among the various methods investigated include the modification of the polymer surface by chemical treatment,[1] rf sputtering processes,[2,3,4] glow discharge,[5] metal evaporation,[6] and others.[7] Among these methods, the sodium etching method has been adapted industrially. Some researchers have investigated the sputtering or surface texturing of fluoropolymers using rf and ion beam sputtering.[8] This investigation uses an ion beam to etch various metals and fluoropolymers for the purpose of improving the adhesive bond strength of the materials when joined to themselves using an epoxy resin. A measurement of the tensile and shear strength of the epoxy-fluoropolymer interface was used to characterize the bond strength. The results of this study are presented herein.

APPARATUS AND PROCEDURE

A 30 cm argon ion source[9] was used to ion beam texture the fluoropolymers and metals. The source, developed from electric propulsion technology, uses a hollow cathode to provide the ionizing current for the ion beam source. Beam extraction is accomplished by a dished, two-grid ion optics system. Neutralization of the beam is achieved by either the use of a plasma-bridge neutralizer,[9,10] using an argon gas cathode, or operating the source grounded and letting secondary electrons, released by ion bombardment of the vacuum facility walls, neutralize the beam.

The vacuum facility, 1.5 m in diameter and 7.3 m long, is sufficiently large to minimize backsputtered facility material from contaminating

the experiments. While the ion source is operating, a background pressure of 4×10^{-5} torr (5.3×10^{-3} Pa) is maintained.

The ion source is capable of operating at beam engeries between 300 and 1500 eV. For the fluoropolymer samples the source energy was 750 eV. The metal specimens were sputter etched at ion energies in the range 950 to 1200 eV (see table I). The fluoropolymers and graphite samples were placed in a holder and the surfaces to be ion beam textured were oriented normal to the ion beam at a location 23 cm from the source grid plane. The nickel, stainless steel and titanium sample surface were also placed in the same position as the fluoropolymers, however, an additional tantalum target was located above and at a 45° angle relative to the metals to provide seeding and sustain surface texturing.[11]

Four fluoropolymers, fluorinated ethylene propylene (FEP), polytetrafluoroethylene (PTFE), perfluoroalkoxy (PFA), and polychlorotrifluoroethylene (CTFE) were first textured and than bonded to themselves using TRA-CON, Inc. TRA-CAST BA-2114 epoxy resin. Target samples were 0.635 cm diameter rod 4.45 cm long for FEP, 1.27 cm rod 4.45 cm long for PFA and 0.635 cm thick sheet for PTFE and CRFE samples. These samples were tapered such that the bonded area was less than the cross sectional area of the specimens themselves. The geometries for the graphite samples (0.635 cm carbon arc rod) was similar to the fluoropolymers. Nickel, titanium (-6Al-4V), and stainless steel type 304 samples were made of flat stock 0.317 cm thick. It should be noted that all of the samples (fluoropolymers and metals) bonded together for this study were bonded using the Tra-Cast® low viscosity epoxy resin. The samples were left to cure for the manufacturer's suggested 72 hours at room temperature to attain maximum bonding strength.

Tensile and shear strength tests were used to characterize the bonding strength of the textured surfaces. Measurements were made using a Wiedemann-Baldwin tensile testing machine using a strain rate of 0.38 mm/minute. The load was applied until the ultimate strength of the epoxy-material interface is reached.

All data presented herein are the average results of testing at least three samples.

RESULTS AND DISCUSSION

Fluoropolymers

Shown in figure 1 are the tensile and shear strengths of bonded PTFE using an epoxy resin after the surface for bonding was prepared in different ways. The weakest bond was, of course, that of the untextured or untreated samples. PTFE was also chemically etched using sodium/napthalene (Matheson's Poly Etch) The results of bonding the PTFE after a chemical etch are also shown in figure 1. The duration of chemical etch and the delay between etching and bonding significantly affects the bond strength as shown in figure 1. The bond strength of PTFE, ion beam textured for 30 minutes prior to bonding, is also shown in figure 1. Since the change in the surface structure of textured PTFE allows a predominatly mechanical rather than a chemical bond[3, 12] there should be negligible time dependance on when the bonding takes place. In this case the ion beam textured surfaces were bonded together 20 days after they were ion beam textured. As shown in figure 1 the tensile and shear strengths of the epoxy resin ion beam textured surface are 46 and 100 percent stronger than those of the respective chemically etched surface.

Figure 2 shows the tensile and shear epoxy bond strengths of four different types of fluoropolymers after ion beam texturing at the same

conditions. PTFE, FEP, and PFA exhibit about the same shear and tensile strengths when bonded with the epoxy resin. CTFE exhibited the highest bond strengths. As can be seen in the scanning electron photomicrographs of figure 3, the surface structure of ion beam textured CTFE shows more widely spaced cone like structure than do the other ion beam textured fluoropolymers, which exhibit closely spaced grass like structure.

To investigate the effect of ion beam exposure time on the tensile strength of fluoropolymers PTFE samples were exposed for various durations. The results of these exposure times are shown in table I. Short exposure times were found to result in a vast improvement over the untextured PTFE tensile strength. The maximum tensile strength occurred with an exposure of 30 minutes. The shortest duration exposure (5 sec at 1200 eV, current density of 1.3 mA/cm^2) resulted in epoxy-material bond tensile strengths of 1060 psi. Scanning electron photomicrographs shown in figure 4 for the various exposure times indicate a change in surface structure and the formation of cones for an exposure time as short as 15 seconds. Whether or not the improved bonding is strictly due to a structural change at the surface or is accompanied by some changes in the surface chemistry[12] warrents further investigation.

The ion beam textured fluoropolymers exhibit properties useful for other potential applications. Some of these applications include the capability of writing on the surface with a pen or pencil, printing on the textured fluoropolymer, decal applications or bonding using adhesive tapes. Another application, which is presently being evaluated, is the use of textured fluoropolymer films as encapsulants for a solar cell using silicone adhesives.

Metals

Nickel, titanium (-6Al-4V), stainless steel type 304 and graphite were exposed at the beam energies and current densities shown in table I. To obtain some surface structure on the metals by texturing, it was necessary to expose the metals for periods of three to four hours. For nickel or titanium, the structure formed after four hours of texturing was not sufficiently large or of the proper roughness to produce an increase in bonding strength over untextured nickel or titanium (see fig. 5). Textured stainless steel and graphite showed large increases in shear strength for stainless steel and equally large increases in tensile strength for graphite when compared to untextured samples. These values are shown in figure 5. The shear strength of the textured stainless steel bond improved by a factor of 3 over untextured stainless steel. Shown in figure 6 is a scanning electron photomicrograph of the textured graphite and stainless steel surfaces. Though the structure of each textured surface appears to be different, apparently there are enough undulations generated by texturing to cause an improvement in bond strength.

CONCLUDING REMARKS

All the fluoropolymers tested showed that ion beam texturing produced superior bond strengths, than could be achieved with conventional surface treatments. CTFE having a widely spaced structure after texturing had the best bond strengths when compared to the other fluoropolymers. When the bond strength of textured PTFE was compared to the bond strength of a sodium/napthalene surface treatment, ion beam texturing was found to produce a superior epoxy bond. It was also shown that ion beam textured surfaces can be stored for extended periods of time prior to bonding without the loss of bond strength typically with chemical etchants.

Textured fluoropolymers provide a rough surface which may be useful for other applications which include: writing or printing, decal applications or bonding using tapes, and as a bonded encapsulant for solar cells.

Textured stainless steel and textured graphite were found to have superior bonding strengths when compared to untextured stainless steel and graphite. Exposure to an ion beam did not sufficiently texture nickel or titanium (-6Al-4V) and therefore did not change the bond strength of these metals.

ACKNOWLEDGEMENTS

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TABLE I. - EPOXY BOND, TENSILE AND SHEAR STRENGTHS OF ION BEAM TEXTURED FLUOROPOLYMERS AND METALS

Sample	Exposure time, min	Exposure energy, eV	Current density, $\mu A/cm^2$	Epoxy bond tensile strength, psi	Epoxy bond shear strength, psi
PTFE	untextured	----	----	183	45
PTFE	1/12	1200	1.3	1060	----
PTFE	1/4	1000	1.0	815	----
PTFE	1/2	750	0.5	1500	----
PTFE	$1\frac{1}{2}$			1510	----
PTFE	3			1550	----
PTFE	6			1550	----
PTFE	18			1630	----
PTFE	30			2050	1050
FEP				2130	1370
PFA				2400	1375
CTFE				3050	2500
Nickel	260	1200	1.0	----	590
Titanium	270	1000	85	----	1335
Stainless steel	270	1000	1.0	----	2875
Graphite	180	950	0.5	3380	----

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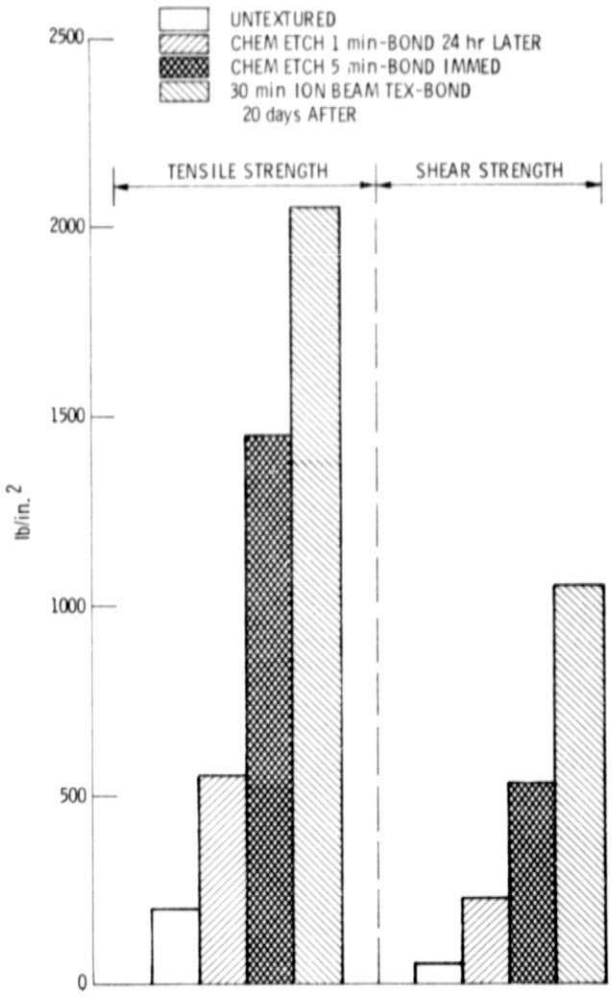

Figure 1. - Tensile and shear strengths of epoxy bonded PTFE. (Bulk tensile strength of PTFE = (3000 to 4500) psi.)

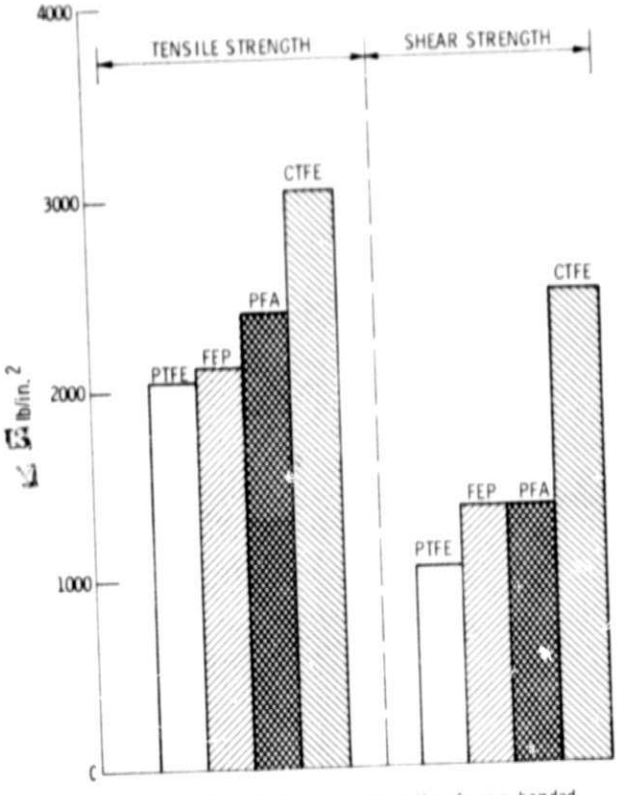

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Figure 2. - Tensile and shear strengths of epoxy bonded ion beam textured fluoropolymers.

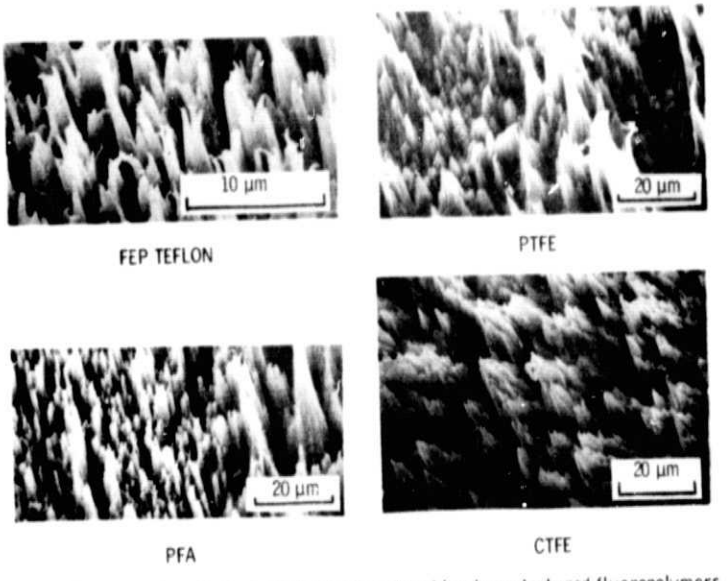
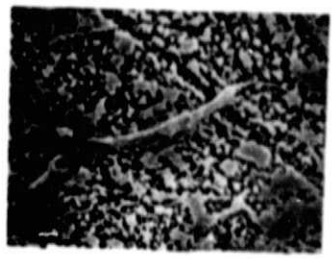
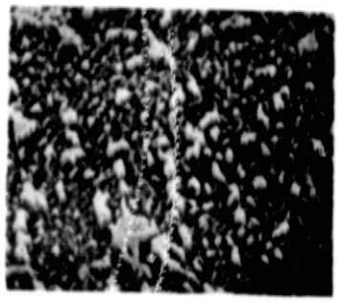


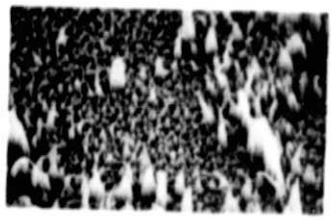
Figure 3. - Scanning electron photomicrographs of ion beam textured fluoropolymers exposed to 0.75 KeV argon ions at 0.5 ma/cm^2 for 30 minutes.



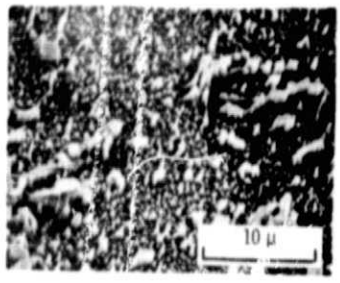
PTFE, 15 SEC EXPOSURE AT 1.0 KeV, ma/cm^2.



PTFE, 5 SEC EXPOSURE AT 1.2 KeV, ma/cm^2.



PTFE, 1.5 MIN EXPOSURE AT 0.75 KeV, 0.5 ma/cm^2.



PTFE, 3.0 MIN EXPOSURE AT 0.75 KeV, 0.5 ma/cm^2.

Figure 4. - SEM of PTFE ion beam textured at different conditions.

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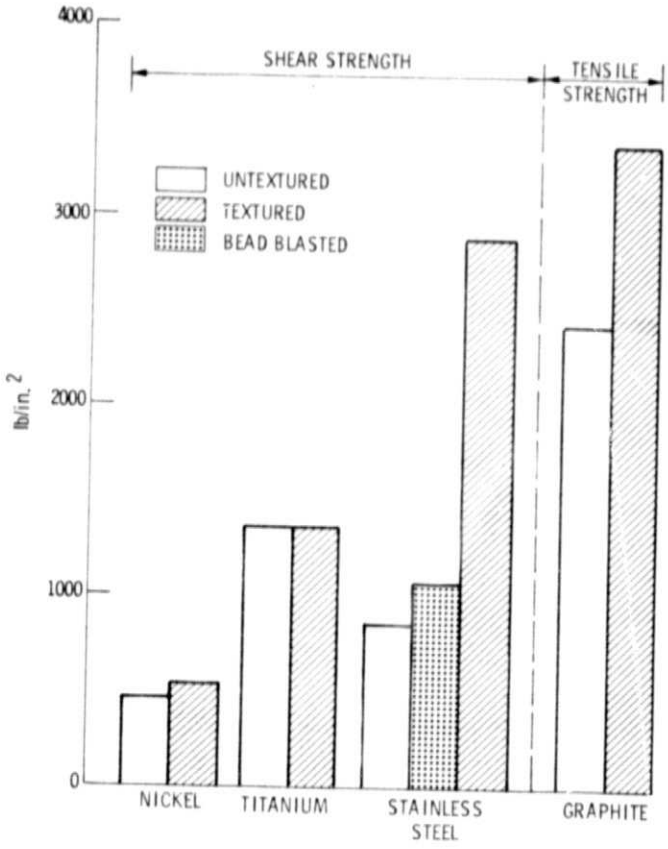
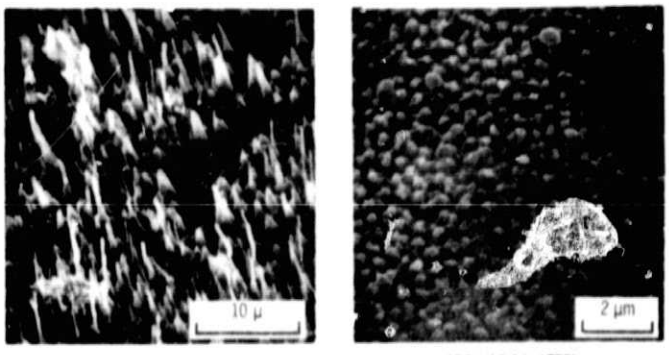


Figure 5. - Epoxy bonded tensile and shear strengths for untextured and textured metals.



GRAPHITE STAINLESS STEEL

Figure 6. - Scanning electron photomicrographs of ion beam textured graphite and stainless steel 30° tilt.

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