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IMPROVED BONDABILITY OF MOLDED RIGID URETHANE FOAM BY PLASMA TREATMENT

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INTRODUCTION

For years it has been recognized throughout the urethane foam industry that molding-to-size is more economical and more reproducible for intricate shapes than is machining. For many applications molded-to-size rigid urethane foam parts are bonded in place. The selection of a mold release is one of the most critical aspects of successful molding operations. The mold release must be easy to apply, must release effectively, and must have no detrimental effects on part quality. The mold release must be nontransferring, or must be readily removed from the molded part, for subsequent bonding or finishing steps.

At The Bendix Corporation, Kansas City Division, the mold release most commonly used in production molding operations, for parts which are not to be bonded, is a wax used alone or as a base coat with a fluorocarbon overspray. Mold releases reported to be nontransferring have been used for parts which are to be bonded. These releases include a silicone glaze, an elastomeric silicone resin, and an elastomeric resin. The nontransferring releases are difficult to apply for parts with tight dimensional tolerances, are difficult to repair in the event they are damaged, or give inconsistent bonding results. One of the new programs at Bendix, which requires a high-temperature molded-to-size polyurethane foam part, specifies use of a nontransferring mold release. Because of previously observed shortcomings of the nontransferring releases, an investigation was undertaken which concentrated on cleanable releases to meet the requirement of bondability.

EXPERIMENTAL

The evaluation scheme consisted of the following tasks: applying the selected mold release, or combination of releases, to the side plates of a test block mold; molding a polyurethane foam block; determining the ease of release; cleaning the block or specimens; and then bonding and testing specimens. A summary of the molding parameters is given in Table 1. BKC 4003-8, a polyester-polymeric isocyanate high-temperature foam, originally specified for production molding, was used for initial evaluation. Because of severe molding problems associated with the use of BKC 4003-8 for production of the part, a polyether-polyisocyanate foam, BKC 44306-10, was used to complete the study. Eleven mold release systems evaluated

were advertised as removable with water or detergent. Thirteen mold releases were evaluated which could not be removed with water.

Plasma treatment was accomplished in one of three units: a commercial 13.6-MHz RF unit; a commercial vacuum unit with a DC power supply; and a Bendix-fabricated AC unit with a 20-kHz power supply. Tensile bond strengths were determined by bonding 28.7-mm-diameter aluminum plugs to the foam specimens, using a room-temperature curing epoxy adhesive, and pulling the bonded assembly on a universal testing machine at 2.5 mm per minute. Shear strengths were determined by bonding foam blocks (Figure 1) with a room-temperature vulcanizing (RTV) silicone rubber, and compressing the assembly at 1.3 mm per minute at 25 or 175°C. Silicone adhesion promoters were applied, as recommended by the manufacturer.

DISCUSSION AND RESULTS

Subjectively, all of the releases excepting one were judged to be almost equal to the Bendix standard wax/fluorocarbon spray in releasing or stripping from the mold side plates. Only the silicone oil/polyvinyl alcohol was more difficult to release than was the Bendix standard release.

Tensile strength assemblies were prepared from specimens in the as-molded condition, in the water- or detergent-washed condition, and in a plasma-treated condition. An argon atmosphere was used for plasma treatment for screening tests. Typical tensile strength data are given in Table 2. The tensile strengths obtained with the releases advertised as water removable are not significantly different from those obtained on as-molded specimens with releases not removable with water. The high results with silicone oil/polyvinyl alcohol and the silicone resin/polyvinyl alcohol are attributed to mechanical bonding to the rough surface and voids. The plasma treatment resulted in significant increases in the tensile strength. In many cases, the adhesive bond strength of treated specimens exceeded the tensile strength of the foam, resulting in failure in the foam specimen. Plasma treatment in argon, oxygen, or air was found to produce similar improvement in the bonding surfaces of molded urethane foams. There were some indications that oxygen produced superior results in shorter cycles.

The production molded parts which required plasma treatment were too large for the laboratory RF unit. Both a DC- and a 20-kHz unit were available for treatment of production parts. Comparable bonding results were obtained with the 13.6-MHz, 20-kHz, or DC-plasma units by adjusting the power and gas flow. In the DC unit, which was used for treatment of most of the production parts, a stepped cycle of increased power levels resulted in diminished arcing and reduced the possibility of damage to the equipment.

The production parts must be shipped from Bendix to another site for bonding into the completed assembly. Therefore, an experiment was conducted to evaluate the effect of aging on the bondability of plasma-treated foam surfaces. Eighty specimens were given an argon/plasma treatment in the RF unit. The specimens were then divided into groups of 10 which were bonded at intervals over a 6-month period. Data on tensile strength are given in Table 3. The bond strength increased slightly after approximately 1 week of aging, then remained relatively constant to 12 weeks. At 24 weeks, a reduction in bond strength of approximately 20-percent was noted. The treatment thus appears to render the surface bondable for a considerable length of time. The increase in strength after aging of 1 week may possibly be attributed to a slow oxygen addition to "free radicals" on the surface of the foam, resulting from the argon plasma. In a more active oxygen atmosphere this effect may not be observed. An experiment to examine this possibility is planned.

After the bonding study had been in progress, it was learned that a resilient high-temperature adhesive was required for the assembly of the production parts. In addition, the loading was ascertained to be mainly shear. A room-temperature vulcanizing rubber was selected as the adhesive. Shear strength specimens were bonded in the configuration shown in Figure 1 and then were tested to failure. The surfaces had been subjected to various treatments.

Average shear strength data from tests at room temperature are listed in Table 4. Oxygen/RF plasma treatment resulted in a 160-percent increase in force required to stress the assembly to failure. However, the failure still occurred at the foam/adhesive interface. In an attempt to achieve greater improvement in the bondability, a primer suggested for increasing the adhesion of RTV rubber to plastic surfaces was applied to the plasma-treated surfaces before assembly with the RTV silicone. Bond failures still occurred, with a reduction in strength to that of untreated foam.

A primer suggested for increasing the adhesion of RTV silicone to metals was then tried. The mode of failure for these specimens was cracking and shearing in the foam at a force exceeding 10 times that of the untreated specimens. Silicone primers for metal surfaces are frequently silanes, which are theorized as coupling to an oxide on the metal surface and then reacting with the silicone adhesive. The oxidized surface of the foam may provide a site for the coupling to occur. A second possibility is that the silicone surfactant in the foam may oxidize to a silica on the foam surface, which would provide a site for the coupling of the primer to occur.

Shear strength data from assemblies tested at 175°C are provided in Table 5. Since a five-fold improvement in room-temperature strength was achieved from use of the silicone primer for metals,

the primer was tried on samples which had not been plasma-treated. Bondline failure occurred at very low strengths. Plasma treatment, in addition to the silicone primer for plastics, again did not result in a significant increase in bond strength or change the mode of failure. Use of the metal silicone primer, which increased the bond strength 15 to 20 fold, still resulted in failure of the foam in the test assembly.

CONCLUSIONS

Most mold releases, including so-called nontransferring releases, interfere with bonding of molded urethane foam. Water-washable mold releases are not readily removable from urethane foams cured at elevated temperatures. Plasma treatment in either argon or oxygen improves the bonding surfaces of molded urethane foam. Comparable bonding results can be obtained with RF (13.6 MHz), AC (20 kHz), or DC-plasma treatments. The plasma-treated foam surfaces will retain the improved bondability for a considerable length of time. Plasma treatment is effective for epoxy and RTV silicone adhesives. A primer recommended for metal bonding with RTV silicone, together with plasma treatment, produces superior bondability of molded urethane foam parts.

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Table 1. Foam Block Molding Parameters

Molding Conditions	BKC 4003-8 (Polyester)	BKC 44306-10 (Polyether)
Base Mold Size* (mm)	177.8 x 177.8 x 25.4	177.8 x 177.8 x 25.4
Density (kg/m^3)	336.4	336.4
Preheat (°C)	43.5	51.5
Cure Cycle (hr at °C)	8 at 163	8 at 163
Strip Temperature (°C)	57.5	57.5

*New aluminum side plates for each release tested

Table 2. Bonding Screening Tests With BKC 4003-8 Foam System

	Tensile Strength (MPa)					
	As-Molded		Washed		Plasma-Treated	
Release System	$\bar{x}$	s*	$\bar{x}$	s	$\bar{x}$	s
Standard Wax/ Fluorocarbon Spray	1.68	0.37			2.63	0.37
Standard Wax	1.63	0.75			2.66	0.26
Fatty Acid Ester	2.04	0.34			2.29	0.35
Silicone Oil	2.16	0.49			1.60	0.45
Silicone Resin	1.88	0.77			2.36	0.34
Water Removable						
Wax 1			1.23	0.51		
Wax 2			1.58	0.44		
Wax 3			0.80	0.23		
Wax 4			0.81	0.34		
Standard Wax/PVA**			0.81	0.37		
Wax 5/PVA			0.54	0.17		
Wax 6/PVA			1.32	0.77	2.33	0.22
Silicone Oil/PVA			2.77	0.33	2.01	0.70
Silicone Resin/PVA			2.23	0.19	2.19	0.15

Adhesive: Epoxy adhesive, cured at room temperature
Specimens: 28.7-mm-diameter foam cylinder, bonded to aluminum plug

*s = Standard deviation

** = Polyvinyl alcohol film

Table 3. Effect of Age on Tensile Strength of Plasma-Treated Foam Surface

Age*	Tensile Strength (MPa) $\bar{x}$	s**
0	2.99	0.73
Hours		
24	2.98	0.81
72	2.94	0.76
Weeks		
1	3.25	0.46
2	3.38	0.37
4	3.43	0.81
12	2.80	0.53
24	2.80	0.53

Mold Release: Standard wax
Material: BKC 44306-10
Treatment: RF Plasma 200 cm^3/minute and argon for 30 minutes at 35 watts

*Ten specimens bonded after plasma-treated surface aged for indicated time, then tensile-tested, using an epoxy adhesive cured at room temperature

**s = Standard deviation

Table 4. Shear Strength Test at Room Temperature

Treatment	Force (N) $\bar{x}$	s*	Result
None	276	111	Bond Failure
Oxygen/RF Plasma	752	405	
Oxygen/RF Plasma and Silicone Plastic Primer	347	93	
Argon/RF Plasma and Silicone Plastic Primer	383	44	Bond Failure
Oxygen/RF Plasma and Silicone Metal Primer	3603	890	Foam Failure

Mold Release: Standard wax
Material: BKC 44306-10
Adhesive: RTV silicone rubber

*s = Standard deviation

Table 5. Shear Strength Test at 175°C

Treatment	Force (N) $\bar{x}$	s*	Result
No Plasma/Silicone Metal Primer	27	4	Bond Failure
Oxygen/RF Plasma and Silicone Plastic Primer	76	31	
Argon/RF Plasma and Silicone Plastic Primer	18	4	Bond Failure
Oxygen/RF Plasma and Silicone Metal Primer	480	98	Foam Failure
Oxygen/DC Plasma and Silicone Metal Primer	676	285	Foam Failure

Mold Release: Standard wax
Material: BKC 44306-10
Adhesive: RTV silicone rubber
Heat Soak: 30 minutes at 175°C prior to test

*s = Standard deviation

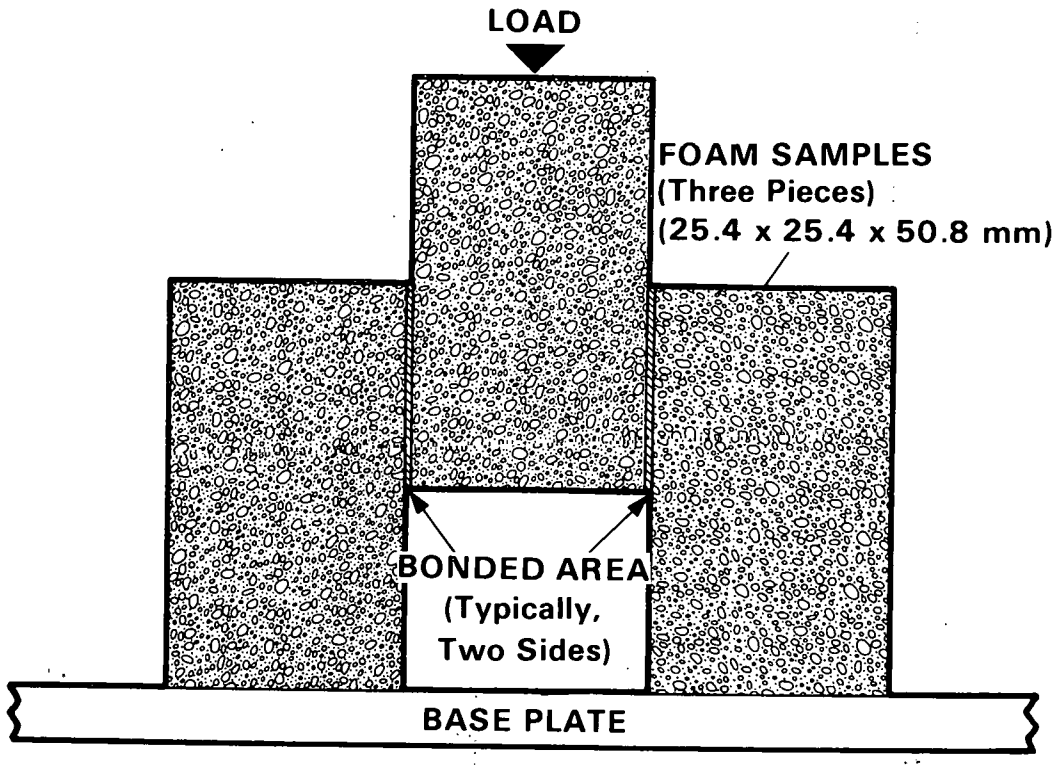

Figure 1. Shear Strength Test of Polyurethane Foam Blocks Bonded With Silicone Rubber