GAS PLASMA TREATMENT TO IMPROVE THE BONDABILITY OF A RTV SILICONE TO FOAMED POLYPROPYLENE

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INTRODUCTION

A chemically blown, injection molded polypropylene foam is used as a support collar. The polypropylene is foamed using 0.5 to 0.7 percent by weight of a nitrogen blowing agent. The collar will be used in an environment which requires that it be coated with a thermal protective material. A RTV coating of 0.0150 ±0.005 in. (0.381 ±0.127 mm) was selected as the thermal protective material. Control of the coating thickness on the polypropylene part is very important. After several methods were considered, it was decided that molding the silicone over the approximately 90 in^2 (581 cm^2) surface was the most efficient. Aluminum molds are used which have cavities slightly larger than the polypropylene part. Mixed and de-aired silicone is injected into the mold where it flows around the part and cures and bonds to the polypropylene. The two-part, vinyl-addition-type silicone was selected because of its reversion resistance, a low viscosity which allows it to be injected into the mold, and its ability to be cured in a confined space.

DISCUSSION

Polypropylene Surface Preparation

Polypropylene is a low surface energy material which is very difficult to wet and bond. Contact angle measurements with distilled water are approximately 90 degrees. The several methods for modifying this surface condition are flame treatment, acid or hot solvent etch, ultraviolet radiation, overcoating, and plasma treatment.

The first three methods were considered impractical. Plasma treatment was considered a likely method but was not fully considered because of problems with production logistics and availability. Overcoating appeared to be a more direct method of surface application and was selected.

Primer Systems for Polypropylene

A chlorinated polyolefin was recommended as having excellent adherence to untreated polypropylene and providing good adhesion between a topcoat and the polypropylene. A primer for the polypropylene was formulated with this material by adding a film forming resin and diluting the mixture in toluene. The formulation contains 25 percent chlorinated polyolefin (10 weight/percent), EVA resin (2.5 weight/percent), and toluene (87.5 weight/percent).

In order to develop the maximum adhesion of the addition-type silicone coating to the part, a silicone primer must be used. Initial development work was performed using the two-primer system with the silicone coating. Each primer was brush applied. The polypropylene primer was cured at room temperature for 0.5 hours followed by 0.5 hours at 180°F (82°C). The silicone primer was cured at room temperature. The relative humidity was monitored to ensure that the silicone primer thoroughly hydrolyzed. Peel (180 degree) and tensile shear tests, using flat sheets of foamed polypropylene, were conducted. Results were encouraging based on the fact that cohesive failures were obtained in the silicone coating. Based on this effort it was decided to attempt production parts.

Coating of Production Parts

Foamed polypropylene parts were routed through the normal production operation and processed according to the following coating procedure:

Wipe parts with trichloroethylene.

Brush apply polypropylene primer (cure at room temperature for 0.5 hours plus 180°F (82°C) for 0.5 hours).

Brush apply silicone primer (cure at room temperature for minimum of 2 hours).

Injection coat and cure RTV silicone in mold (cure at 180°F (82°C) for 1 hour).

Some parts were completely bonded and cured; however, most parts were unsatisfactory and would be rejected. The silicone adhesion was determined by peeling 1-inch-wide (25 mm) strips of coating from the polypropylene. The results are reported in pounds per inch (ppi) of width (kg/25 mm). A summary of the results is presented in Table 1. After making numerous parts it became obvious that the same problems were reoccurring. These were erratic adhesion across the part, local inhibition (uncured) of silicone, and no adhesion of silicone to polypropylene.

Because of these poor results, a two-pronged attack was undertaken to eliminate the reoccurring problems. One effort was directed towards analyzing the polypropylene and its surface to determine whether contamination was a problem, especially in light of the fact that a blowing agent which decomposes is used. The second effort was directed at obtaining some fundamental data on the individual primers and the silicone coating. No data was available on the adhesion (maximum peel strength) of the RTV silicone on aluminum or on solid polypropylene.

Table 1. Reproducibility of Adhesion of RTV Silicone to Polypropylene Using 180-Degree Peel Test

	Peel Strength		
Part Definition	Maximum (ppi) (kg/25 mm)	Minimum (ppi) (kg/25 mm)	Average (ppi) (kg/25 mm)
Parts primed in production area and coated in engineering laboratory	5 (2.27)	1 (0.5)	2.5 (1.1)
	4.7 (2.1)	2.5 (1.1)	3.5 (1.6)
Parts primed and coated in engineering laboratory	4 (1.8)	0.5 (0.2)	2 (0.9)
	3 (1.4)	1.2 (0.5)	2 (0.9)
Parts primed and coated in production area	3.5 (1.6)	1.5 (0.7)	2 (0.9)
	4.5 (2)	3 (1.4)	3.5 (1.6)
	4.2 (1.9)	3 (1.4)	3.5 (1.6)
	8 (3.6)	4 (1.8)	6 (2.7)
	7 (3.2)	1.5 (0.7)	3 (1.4)
	5 (2.27)	2 (0.9)	3 (1.4)
	7.5 (3.4)	5.5 (2.5)	6.5 (3)
	2.8 (1.3)	1.5 (0.7)	2 (0.9)
	9.5 (4.3)	1.5 (0.7)	2 (0.9)

Contamination Characterization

Contact angle analysis with distilled water was made on new, foamed polypropylene parts and found to uniformly yield 90 degree angles. This angle is considered normal for polypropylene. In contrast, all parts analyzed immediately before preparing for the coating process, several weeks later, showed considerable non-uniformity in contact angles, indicating contamination. Values ranged from 30 to 90 degrees across the part. Large deviations on the edges were particularly apparent.

The blowing agent, shown in the following listing, along with its decomposition products have an extremely high solubility parameter of about 18. This dictated that a highly polar solvent such as water or alcohol is needed to remove any residual blowing agent or its decomposition products.

Blowing Agent

- Chemical composition: Azodicarbonamide
- Decomposition gas (percent): 65 N_2
24 CO
5 CO_2
5 NH_3
- Solid decomposition products: Urazon
Biurea
Cyamelide
Cyanuric acid

Samples of the foamed polypropylene were soaked in water, trichloroethylene, and a blend of solvents identified as solvent blend C. The liquids were analyzed by mass spectrograph. The results are reported in Table 2 and are interpreted to be detergent, blowing agent decomposition products, and polypropylene plasticizers.

Several foamed polypropylene production parts were obtained and their surfaces were checked for contamination by contact angle measurements. Various contact angle measurements ranging from 30 to 90 degrees were obtained. The contaminated surfaces were scrubbed in distilled water for several minutes and rinsed in water and isopropyl alcohol. Contact angle measurements were again made over the entire part. Consistent 90 degree readings were obtained indicating that water effectively removed the contaminants.

Table 2. Mass Spectra Analysis of Polypropylene Surface Contaminants After Water and Solvent Soaking

Solvent	Contaminant: Major	Contaminant: Minor
Trichloroethylene	Butylated hydroxyl toluene	Stearic acid
Solvent blend*	Stearic acid	Palmitic acid (polypropylene additive)
Water	Urea	Cyanic acid

*Percent by volume of methylchloroform (17), n-butyl acetate (33), trichloroethylene (33), and isopropyl alcohol (17).

Adhesion Characteristics of Silastic J

As part of the investigation into the poor quality bond adhesion of the RTV silicone molded to foamed polypropylene it was decided to investigate the adhesion characteristics of the silicone to solid polypropylene and to aluminum. Previous work had not determined what the maximum peel strength between the silicone and foamed polypropylene could be.

Silicone Adhesion to Aluminum

Peel test specimens were prepared using aluminum sheet stock material. All samples were vapor degreased before application of the silicone primer. One set of samples had previously been scruff sanded. Each test sample had the silicone trowelled on it and a 1-inch-wide (25 mm) piece of silicone-primed fiberglass cloth potted into the silicone. Three different cure cycles were used. After cure, cuts were made in the silicone alongside the edges of the fiberglass tape. Peel tests were made using a tensile testing machine. The results are reported in Table 3. All failures were cohesive in the silicone at a peel strength of approximately 13 pounds per inch (ppi) (5.9 kg/25 mm) of width. Varying the temperature and time did not influence the results.

Silicone Adhesion to Solid Polypropylene

Various methods for applying the polypropylene and silicone primers were evaluated. These included brushing, spraying, and dipping. No outstanding peel strength results were obtained. During the course of applying the two primers, it became obvious that something had to be done to the polypropylene surface to remove the gloss finish and improve primer wetting. This was accomplished by abrading the surface with 240 grit paper. Also, it was found that the film forming component (EVA resin) of the polypropylene primer was soluble in the silicone primer solvent (VM & P Naptha). Various surface preparation procedures were selected and tried on pieces of solid polypropylene. Again, peel strength specimens were prepared and tested. Table 4 presents a summary of the surface preparation techniques and accompanying results. As can be seen from this data, the best results were obtained with an oxygen-plasma-treated surface, coated with the silicone primer only, and the silicone cured at 180°F (82°C) for 1 hour. Oxygen-plasma-treated specimens using both primers did not provide acceptable strength values.

Plasma Treating Polypropylene

Table 5 presents a test matrix of specimens prepared using different plasma treatments. Plasma atmosphere, chamber time, and treated specimen shelf life were the parameters evaluated. One set of specimens was cured at room temperature for 24 hours. All other specimens were cured at 180°F (82°C) for 1 hour. The results of the 180-degree peel tests are reported in Table 6. Plasma treatment with argon atmosphere did not improve the adhesion of silicone to polypropylene. Reducing the time in oxygen plasma treatment from 30 to 10 minutes did not affect the adhesion of the silicone. Applying and curing the silicone on plasma treated parts up to 7 days after plasma treatment did not reduce the silicone adhesion. All specimens with peel strengths in the 10 to 15 ppi (4.54 to 6.8 kg/25.4 mm) range exhibited cohesive failures in the silicone (the expected strength for the silicone).

Polypropylene samples were treated in an oxygen plasma at 100 watts for 30 minutes and their contact angles were monitored with distilled water over a 2 week period. The results were 50 degrees within 3 hours after plasma treatment, 58 degrees after 3 days, and 60 degrees after 7 days and also after 2 weeks. This data indicates that a good contact angle is maintained for an extended time, and it agrees with the peel strength results reported in Table 6 that the polypropylene can be stored after treatment and then successfully coated.

Table 3. Adhesion of RTV Silicone to Aluminum With Silicone Primer

Cure of Silicone	Peel Strength* (ppi) (kg/25 mm)
Vapor Degrease	
Room temperature for 24 hours	13.8 (6.3)
Room temperature for 24 hours	11 (5)
160°F (71°C) for 1 hour	14.6 (6.6)
160°F (71°C) for 1 hour	9.4 (4.3)
200°F (93°C) for 5 hours	12.8 (5.8)
200°F (93°C) for 5 hours	
Sand and Vapor Degrease	
Room temperature for 24 hours	13.8 (6.3)
Room temperature for 24 hours	12.5 (5.7)
160°F (71°C) for 1 hour	13 (5.9)
160°F (71°C) for 1 hour	13.9 (6.4)
200°F (93°C) for 5 hours	14 (6.4)
200°F (93°C) for 5 hours	12.5 (5.7)

*All failures were cohesive in silicone.

Table 4. Peel Strength of RTV Silicone to Solid Polypropylene

Surface Preparation	RTV Silicone Cure	Breakaway Strength (ppi) (kg/25mm)	Running Strength (ppi) (kg/25mm)
240 grit abrade Trichloroethylene silicone primer only	180°F (82°C) for 1 hour and room temperature for 24 hours	0.5 (0.2) 0.3 (0.1)	0.2 (0.1) 0.2 (0.1)
Trichloroethylene Polypropylene primer and silicone primer	Room temperature for 24 hours	1.8 (0.8) 1.3 (0.6)	0.7 (0.3) 1 (0.5)
240 grit abrade Trichloroethane Polypropylene primer and silicone primer	Room temperature for 24 hours	0.75 (0.3) 1.75 (0.8)	0.5 (0.3) 0.75 (0.34)
240 grit abrade Trichloroethylene Polypropylene primer and silicone primer	180°F (82°C) for 1 hour and room temperature for 24 hours	12 (5.5) 12 (5.5)	4 (1.8) 4 (1.8)
240 grit abrade Trichloroethane Polypropylene primer and silicone primer	180°F (82°C) for 5 hours and room temperature for 24 hours	4 (1.8) 11 (5)	4 (1.8) 10-4 (4.5-1.8)
Trichloroethylene Oxygen plasma Polypropylene primer and silicone primer	Room temperature for 24 hours	1.75 (0.8) 2 (0.9)	0.8 (0.4) 2 (0.9)
Trichloroethylene* Oxygen plasma and silicone primer only	180°F (82°C) for 1 hour and room temperature for 24 hours	13 (5.9) 16 (7.3)	12-10 (5.5-4.5) 14-8 (6.4-3.6)

*All failures were silicone to plastic except this surface preparation which failed silicone to silicone.

Table 5. RTV Silicone to Solid Polypropylene Bonding Test Specimen Matrix Evaluation of Plasma Treatment

Operations	Specimen Configuration								
	A	B	C	D	E	F	G	H	I
Trichloroethylene Wipe	x	x	x	x	x	x	x	x	x
Plasma clean									
Oxygen; 100 watts, 30 minutes at 0.5 torr (67 Pa) and	x	x				x	x	x	xxx
10 minutes at 0.5 torr.			x						
Argon; 30 watts 30 minutes at 0.25 torr (33 Pa) and				x					
10 minutes at 0.25 torr.					x				x
Polypropylene primer, brush and cure at 180°F (82°C) at room temperature for 1 hour.						x			x
Silicone primer, brush and cure at room temperature for 1 hour	x	x	x	x	x	x	xx	xxx	x
RTV Silicone, 10/100, cure at room temperature for 24 hours and 180°F (82°C) for 1 hour	x	x	x	x	x	x	x	x	x

xxTwo days between plasma treatment and primer application.
xxxFive to seven days between plasma treatment and primer application.
xxxxApply polypropylene primer and cure, then apply silicone primer and cure and then plasma treat.

Table 6. Peel Strength Results of Silicone Bonded to Plasma Treated Polypropylene

Configuration	RTV Silicone Cure	Peel Strength (ppi) (kg/25 mm)	Failure Location
A	Room temperature	10 (4.54)	Cohesive in silicone
A	for 24 hours	13 (5.9)	Cohesive in silicone
B	180°F (82°C)	12 (5.5)	Cohesive in silicone
B	for 1 hour	12 (5.5)	Cohesive in silicone
C	180°F (82°C)	9.6-14.7 (4.4-6.7)	Cohesive in silicone
C	for 1 hour	9.2-14.5 (4.1-6.5)	Cohesive in silicone
D	180°F (82°C)	0.2 (0.1)	Silicone to plastic
D	for 1 hour	1.1 (0.5)	Silicone to plastic
E	180°F (82°C)	0.6 (0.3)	Silicone to plastic
E	for 1 hour	0.6 (0.3)	Silicone to plastic
F	180°F (82°C)	2.6 (1.2)	Silicone to plastic
F	for 1 hour	3.6 (1.6)	Silicone to plastic
G	180°F (82°C)	13 (5.9)	Cohesive in silicone
G	for 1 hour	14 (6.4)	Cohesive in silicone
H	180°F (82°C)	11.5 (5.2)	Cohesive in silicone
H	for 1 hour	12 (5.5)	Cohesive in silicone
I	180°F (82°C)	5.8 (2.6)	Silicone to plastic
I	for 1 hour	5.5-12.8 (2.4-5.8)	Silicone to plastic

Approximately 15 ppi (6.8 kg/25 mm) of peel strength can be expected between the RTV silicone and oxygen-plasma-treated polypropylene based on the results obtained from the adhesion study. Silicone primer is necessary; however, a polypropylene primer coat can be deleted. Test data has shown that storage of plasma treated parts up to 7 days is permissible without significant degradation in silicone peel strength. No correlation was found between peel strength and cure time or temperature; however, room temperature cured parts show signs of tacky surface or inhibition on some parts.

Processing of Production Parts

Based on the information obtained in two studies of contamination and adhesion, ten production parts were processed. A flow chart of the various operations is presented in Figure 1. The polypropylene primer overcoat was eliminated. The first two specimens were plasma treated at 400 watts in the oxygen plasma for 2 hours. Some melting on thin sections occurred. Therefore, the power level was cut back to 200 watts for 1 hour. The remaining parts were treated at this plasma setting and coated with the silicone. Upon removal from the molds, all silicone coated parts were totally bonded and were completed cure.

Six of these parts were sectioned and had additional silicone and the 1-inch-wide (25 mm) fiberglass tape applied. They were then peel tested to determine the silicone adhesion to the polypropylene. The results, as reported in Table 7, were considered satisfactory. Based on these results, a viable and repeatable process was considered to be developed.

SCRUB PART THROUGHLY IN DISTILLED WATER

RINSE IN DISTILLED WATER

FLUSH WITH ISOPROPYL ALCOHOL

PLASMA TREATMENT

OXYGEN ATMOSPHERE

200 WATTS POWER

1 TORR PRESSURE

1 HOUR TIME

BRUSH APPLY SILICONE PRIMER AND AIR CURE FOR 2 HOURS

APPLY CATALYZED SILICONE AND AIR CURE FOR 1 HOUR

Figure 1. Flow Chart of Processing Sequence for Production Parts

Table 7. Silicone Adhesion to Plasma Treated Production Parts

	Peel Strength	
Specimen	Breakaway (ppi) (kg/25 mm)	Running (ppi) (kg/25 mm)
1	9 (4.1)	7 (3.2)
2	7 (3.2)	6.5 (3)
3	10 (4.5)	5.5 (2.5)
4	8.5 (3.9)	7 (3.2)
5	11 (5)	8 (3.6)
6	11 (5)	6 (2.7)