EVALUATION OF URETHANE ADHESIVE-COMPOSITE JOINTS UNDER DIFFERENT ENVIRONMENTAL CONDITIONS

J.G. Quini*[1,2] G. Marinuci[2]

[1] Masterpol Adhesives Technology
R. Luiz Vaz de Camoes, 98 - ZIP CODE 07210-007 – Sao Paulo – Brasil
josuequini@hotmail.com, http://www.masterpol.com.br
[2] Nuclear and Energetic Research Institute – IPEN/CNEN-SP
Av. Prof. Lineu Prestes, 2242 – ZIP CODE 05598-9000 – São Paulo – Brasil
Department of Materials Technolgy
marinucci@ipen.br, http://www.ipen.br

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Abstract

Structural adhesives technology has changed the concept of joints bonding different materials in a unique solid assembly and making them part of the structures. These joints not only increase strength and stiffness but also reduce weight, which is important, for instance, for vehicles and airplanes. The present study reports the results of applying urethane structural adhesives in automotive components. RTM, SMC, ABS thermoplastic and galvanised steel samples was evaluated under temperaturem time, humidity and destilled water. The results show very good adherence between the adhesive and the substrates under these conditions.

1. Introduction

In recent years, the structural adhesives technology has shown great potential application because of its ability to transform complex structures into solid, monolithic units using different materials. Therefore, joints become part of these structures, providing, in addition to weight reduction, a considerable increase in mechanical strength and stiffness[1].

The adhesives for such applications have attractive chemical and mechanical properties, which have not been sufficiently studied or understood, perhaps because of the complex interactions existing between the substrate and adhesives[2]. Theories based on adsorption, diffusion, mechanical lock, chemical interactions and electrostatic forces and secondary adhesive interface – substrate are available[3].

The use of structural adhesives in vehicles arose from the need to bond metallic inserts and reinforcements in hoods, grilles and fenders to components manufactured by the RTM and SMC processes without mechanical fasteners. The success of structural adhesives has changed the concept of structural bonding, and today, almost all vehicles use structural adhesives such as urethane, epoxy and acrylic[4]. Polymeric adhesives offer several advantages over metallic joints, providing uniform distribution of static and dynamic stress and cost reduction in the production chain and in maintenance, as compared with traditional mechanical fasteners[5].

The use of composite materials bonded with structural adhesives has recently experienced great demand, as the adhesives are able to join different materials effectively and irreversibly, including mechanical fastening systems[6,7].Notably, the mechanical fixing can promote delamination in composites, which can be catastrophic and, depending on the temperature of exposure and the differences in the thermal expansion coefficients between the parts, can give rise to high tension at the joint, compromising the integrity of the composite[8]. Thus, the shear strength of joints bonded with adhesive urethane should be studied at different temperatures to which the joint could be continuously or momentarily exposed.

2. Materials

To manufacture the specimens, the adhesive Masterpur Structural 300 was applied using a pneumatic machine that performs dosage and mixing of the two components of the adhesive. The mixing ratio by weight of the two components was 100 parts of component A to 25 parts B component, as recommended by Masterpol Adhesives. The substrates were composites made of unsaturated polyester and glass fibres. The composites were moulded by the RTM and SMC processes, both widely used in automotive parts. The volume fractions were 70% and 30% for the polymer matrix and glass fibre, respectively. In many cases, there is a combination of adhesive urethane in joints with composites, metals and ABS thermoplastics.

According to the procedures defined in ASTM 3163 for composites, metals and plastics, the specimen dimensions were set to 25 mm wide and 100 mm long. The area of the adhesive was 25 x 25 mm. The surface was prepared by abrasion to remove the surface layer. This practice is necessary for the removal of mould residue that can interfere with the adhesion of the urethane. A supplementary cleaning with trichlorethylene was also performed to remove the dust produced by grinding. The samples on the metal and ABS substrates treated by plating and black chroming were only cleaned with trichloroethylene to remove dirt or grease from the surface.

Bonding was performed after the plates had been cut, sanded and cleaned with solvent. A small amount of adhesive urethane was applied, about 2 g per specimen, previously dosed and mixed with the applicator and metering equipment. Next, about four 0.7 mm balls of zirconium were placed to define the thickness of the adhesive. The control of the adhesive thickness is necessary because it is known that the mechanical strength of a joint can vary depending on the thickness of the adhesive. After 24 hours, the time needed to cure the adhesive urethane, the specimens were ready to be tested.

The test consisted of holding the specimen in the equipment grip and then accelerating it to a constant speed of 12.7 $mm.min^{-1}$ until the complete separation of the two substrates. The maximum load was recorded to calculate the maximum shear strength. These tests are designed to determine the strength of the adhesive joint with under normal to salt spray.

3. Results and Discussion

3.1. Effect of temperature, time and relative humidity on bond strength

Relative humidity can initiate hydrolysis and degradation in many polymeric materials. Thus, it is important to evaluate the effect of humidity and temperature on the different joints exposed to these conditions, allowing for the prediction of the behaviour of the joint when it is in use.

Shear strength tests were conducted with exposure of the specimens to condition 1 – exposure for 500 h, at 25 °C and 98% relative humidity and condition 2 – exposure for 500 h, at 38°C and 98% relative humidity. The test results are shown in Table 1 and Table 2 for SMC, RTM, ABS and galvanised carbon steel, under the conditions mentioned above.

Table 1. Shear strength of specimens in SMC, RTM, ABS and galvanized carbon steel, set out in condition 1 - exposure for 500h at 25 ° C and 98% relative humidity.

Substrate	Shear Strength (MPa) - condition 1	Expanded Uncertainty	Variation (%)	Form of rupture
SMC	5.3	0.2	-8.6	Specimen
RTM	5.7	0.4	-6.6	Specimen
ABS	3.3	0.1	-8.3	Specimen
Galvanized carbon steel	10.5	0.5	-1.9	Cohesive

Table 2. Shear strength of specimens in SMC, RTM, ABS and galvanized carbon steel, set out in condition 2 - exposure for 500h at 38 º C and 98% relative humidity.

Substrate	Shear Strength (MPa) - condition 2	Expanded Uncertainty	Variation (%)	Form of rupture
SMC	3.2	0.1	-44.8	Delamination
RTM	3.2	0.3	-47.5	Delamination
ABS	2.4	0.2	-33.3	Specimen
Galvanized carbon steel	11.1	0.4	3.7	Cohesive

For all samples using polymeric substrates, SMC, RTM and ABS, a reduction in the shear strength was identified, always with failure in the substrate, when compared with that obtained at baseline (25 °C), as shown in Table 3, which also indicates the weakening of these substrates.

TABLE 3. Evaluation of shear strength of joints.

Substrate	Shear Strength (MPa)	Expanded Uncertainty	Form of rupture
SMC	5.8	0.4	Delamination
RTM	6.1	0.3	Specimen
ABS	3.6	0.1	Specimen
Galvanized carbon steel	10.7	0.4	Cohesive

For the SMC substrate tested under condition 1, there was a reduction in shear strength of 8.6%, with rupture of the specimen; under condition 2, a reduction of 44.8% with delamination was observed. For RTM under condition 1, there was a decrease of 6.6%, with rupture of the specimen and under condition 2, a reduction of 47.5% with delamination. In the composite substrate, it was observed that not only the reduction behaviour of the shear strength was similar in shape to the rupture but also the percentage of reduction, and thus the combined effect of exposure to temperature and relative humidity significantly reduces the shear strength of the joint for these composite materials.

In ABS substrates subjected to condition 1, there was a reduction of 8.3% in the shear strength, while under condition 2 there was a reduction of 33.3%. The behaviour of ABS under these two conditions was similar to that observed in composite substrates.
Again, the resistance of the galvanised steel substrate could be observed separately from the mechanical behaviour of the adhesive. Despite the effect of humidity on the urethane adhesive being limited to the side edges, it actually occurs, though to a lesser extent, because much of the contact area of the adhesive is protected by the substrate.

Under condition 1, the shear strength was reduced by 1.9%, with cohesive failure; under condition 2, there was an increase in the shear strength of 3.7%, also with cohesive failure. This result shows that the ambient temperature of 25 ºC and the relative humidity had little effect on the adhesive. However, relative humidity combined with a temperature of 38 ºC led to a post-curing process that made the adhesive urethane tougher. This behaviour of the adhesive is opposite to that observed in the polymeric substrates.

3.2. Effect of immersion in distilled water on the shear strength

The immersion of polymeric materials in water may initiate hydrolysis and corrosion and reduce the resistance of a joint, which may affect the substrate and the urethane adhesive. This condition may occur in a practical situations: for example, bonded parts of vehicles will be exposed to water in the form of rain or cleaning purposes. Therefore, the effect of water immersion on the joints of SMC, RTM, ABS and galvanised carbon steel was evaluated.

The specimens were immersed in distilled water at 25 °C for 500 h, followed by manual drying with paper towels, and were tested to obtain the shear strength. Distilled water was used instead of drinking water as per standardised testing; it is known that depending on the location, the composition of dissolved salts in drinking water vary significantly. The results are shown in Table 4.

Table 4. Shear strength of specimens in SMC, RTM, ABS and galvanized carbon steel after 500h immersion in distilled water at 25 ° C.

Substrate	Shear Strength (MPa) - 500h after immersed in distilled water 25 º C	Expanded Uncertainty	Variation (%)	Form of rupture
SMC	4.7	0.2	-19.0	Specimen
RTM	5.1	0.3	-16.4	Specimen
ABS	3.1	0.1	-13.9	Specimen
Galvanized carbon steel	11.0	0.4	2.8	Cohesive

Similar to what happened to the joints exposed to humidity, the specimens of polymeric substrates, SMC, RTM and ABS showed a reduction in shear strength, always with failure in the substrates, when compared with the initial conditions at 25 °C shown in Table 3; this indicates that there was a weakening of these substrates.

The SMC substrate samples had their shear strengths reduced by 19.0%, and the RTM shear strengths were reduced by 16.4%. ABS showed a reduction of 13.9%, and all specimens exhibited rupture. Unlike of the polymeric materials joints, those ones of the galvanized steel joints showed an increase in shear strength of about 2.8%, but in this case, the urethane adhesive was partially protected from contact with distilled water.

3.3. Effect of salt spray on the shear

One of the most critical factors for promoting degradation of polymeric materials and corrosion of metallic materials, with consequent loss of material strength, is the exposure to salt spray. Because of the presence of minerals, salt spray can combine the corrosive effects of minerals with moisture, reducing the lifetimes of many materials. The effect of salt spray on the joints, previously mentioned in the exposure condition for 240 h, was evaluated. The results of the tests are shown in Table 5.
There was a reduction in shear strength for all the joints, when compared with the results obtained under the initial condition at 25 ° C, as shown in Table 3. The reductions were much higher in the

polymer substrates, with reductions of 44.8% for SMC, 49.2% for RTM and 38.9% for ABS, all showing specimen failure.

In joints composed of galvanised carbon steel, the shear strength was reduced by only 0.5%; this reduction occurred through the weakening of the adhesive because the substrate did not suffer significant corrosion. The observed reduction was, however, relatively small because of the limited exposure of the adhesive, which occurred only on the specimen sides.

Table 5. Shear strength of specimens in SMC, RTM, ABS and galvanized carbon steel after exposure of 240 hours in salt spray.

Substrate	Shear Strength (MPa) - 240 hours after exposure to salt spray	Expanded Uncertainty	Variation (%)	Form of rupture
SMC	3.2	0.1	-44.8	Delamination
RTM	3.1	0.1	-49.2	Delamination
ABS	2.2	0.1	-38.9	Specimen
Galvanized carbon steel	10.65	0.5	-0.5	Cohesive

4. Conclusion

The evaluation of the relative humidity effect at 25 ºC showed a reduction in shear strength in all joints, but when the exposure occurred at 38 ºC the galvanised carbon steel joints showed an increase in the shear strength because of the post-curing of the adhesive and the protection of the adhesive by the substrate.

Immersion in distilled water reduced the shear strength of SMC, RTM and ABS joints. This reduction might be due to the hydrolysis of the substrate, as suggested by the failure by rupture. The metal joint was protected from oxidation by the galvanised carbon steel coating, therefore there was a small increase in shear strength with cohesive failure such that the adhesive urethane resisted direct exposure to distilled water.

Exposure to salt spray, even at a temperature of 25° C, reduced the shear strength of all of the joints. In SMC, RTM and ABS samples, the reduction was greater than 40 %, whereas the galvanised carbon steel joint presented a reduction of only 0.5 % because the exposition area was small.

Notably, in all exposure conditions, SMC, RTM and ABS substrates experienced reduction in their hear strengths, while the adhesive increased its load-bearing ability. Reductions in the shear strength of all polymeric substrate joints were observed, whereas in galvanised carbon steel joints some increases in shear strength were observed.

It was found that the urethane adhesive endured the deleterious effects of conditioning of the SMC, RTM and ABS substrates, thus providing a useful battery of test conditions through which to evaluate similar mechanical components, as it was concluded that the joints would be of limited use given the mechanical limitations of the substrates. It should also be noted that these constraints have been proposed as standards for adhesives manufacturers aiming to analyse these extreme conditions together, as they are likely to occur during the joint lifetime.

The results support the conclusion that the urethane structural adhesive has excellent adherence to all of the substrates tested in this study. In composites and thermoplastic joints, the lap shear was limited by the resistance of the substrate, and in metal joints, the failure was in the adhesive. Also, there is evidence that the adhesive undergoes a post-cure at higher temperatures. In metal joints, cohesive failure was observed.

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