Progress in Organic Coatings 80 (2015) 120–141

Contents lists available at ScienceDirect

Progress in Organic Coatings

journal homepage: www.elsevier.com/locate/porgcoat

Review

Chemical adhesion of silicone elastomers on primed metal surfaces: A comprehensive survey of open and patent literatures

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ARTICLE INFO

Article history:
Received 12 September 2014
Received in revised form
26 November 2014
Accepted 27 November 2014
Available online 23 December 2014

Keywords:
Adhesion
Silane
Silicone elastomer
Metal
Primer
Coatings

ABSTRACT

The main objective of this review is to compile information regarding the chemical adhesion of silicone elastomers on primed metal surfaces. It additionally aims at giving some hints to formulate primer formulations, according to the mechanical and environmental properties targeted in the manufacture of composite parts. We first cover briefly the fundamental aspects of adhesion, the different mechanisms of strong and durable bonds generated using a primer, the various organosilanes employed as adhesion promoters for silicone elastomers on metals and the principle mechanical tests used to characterize the adhesive properties of composite parts. A complete description follows on the choices of solvent-based silane cocktails according to the nature of silicone elastomers to be stuck, namely free-radical, addition and condensation cured systems. Simple to complex mixtures are covered, as well as original patented approaches to adhere silicone to metals.

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http://dx.doi.org/10.1016/j.porgcoat.2014.11.022
0300-9440/

1. Introduction

Metal/silicone composites are often found in automotive and aerospace industries for the production of technical parts such as dampers, seals, ... Silicone elastomers are generally preferred over conventional elastomers for their intrinsic resistance properties against UV, high temperature, solvents and, in a lesser extent, to ozone. Theoretically, physical intermolecular interactions between PDMS and polar surfaces would provide sufficient adhesion: the teams of Creton [1–3] and Vallat [4,5] observed debonding energies between PDMS films and a glass substrate typically on the order of few J m^{-2} [6]. Still, strong adhesion of the silicone elastomer onto a substrate, e.g. glass, metals, plastics, fabrics, is sought for the composite parts to maintain a high stress under severe environmental conditions. Physical intermolecular forces across the interphase are clearly not sufficient and thus require to be coupled with chemical (strong) links [7].

Covalent bonding of silicone elastomers on metallic substrates is not easy because of an incompatible surface chemistry. Adhesion must be promoted by the use of coupling agents of several types such as e.g. organotitanates, amide/imides, zircoaluminates, organosilanes, ...This last category is particularly interesting because of its chemical compatibility with silicones [8,9]. Silanes can be used as adhesion promoter in the silicone system and/or as pre-treatment for the substrate, as a primer. Direct addition of organosilanes in the silicone delivers self-priming systems, that have been reported in the literature [10–23]. The advantage of which is a simple processing but the difficulty of which lies in the necessity of organosilanes migration toward the interface between the silicone elastomer layer and the substrate to generate effective adhesion [24]. Also, the manufacture of most technical parts composed of a metal substrate and a silicone elastomer are produced in a mold, under pressure and at high temperature; the self-priming systems cannot be applied to avoid difficult unmolding. We will not further consider these systems in this review. In a primer, the silane coupling agent(s) is (are) applied to the inorganic substrate before the product to be adhered is applied. By using the right organosilane or mixture of it, a poorly adhering paint, coating, sealant or rubber can be converted to a material that will frequently maintain adhesion even when subjected to severe environmental conditions (e.g. high temperature, underwater immersion or UV radiation) [24]. The main disadvantage of priming the substrate is the extra-step added to the whole process of the composite manufacturing, which brings its own problems and cost.

Many reviews have been written about the role of silanes as coupling agents and their particular chemistry [9,25–33]. Still, we did not find reviews describing the adhesion of silicone elastomers on primed metal surfaces. This paper aims at fulfilling this apparent lack of literature survey and to present synthetically the different ways to formulate a primer for sticking a silicone elastomer on a metallic surface. In the first chapter, we summarize the various basics to be known to consider studying adhesive properties in general, namely the fundamental aspects of adhesion, the principal mechanisms of adhesion, the chemistry of organosilanes, the metal treatments and its surface characterization and the mechanical tests devoted to adhesion measurements. In a second part, we exhaustively describe the numerous (patent) reports that have been made on the use of primers to adhere silicone elastomers, according to their mode of vulcanization. Simple to very complex cocktails are described, together with various original tricks to favor adhesion of any kind of silicones on metallic surfaces.

2. Basics for studying adhesion

2.1. Fundamental aspects of adhesion

The reversible work of separation under equilibrium conditions for two different materials which do not react chemically nor have specific interactions, is given by the surface free energies of the free components. This work of adhesion is expressed by the following relationship (Eq. (1)) for detachement in vacuo, or in an inert atmosphere:

$$-U_{12} = W_A = \gamma_1 + \gamma_2 - \gamma_{12} \quad (1)$$

with γ_1 and γ_2 corresponding respectively to the specific surface energies of the materials 1 and 2 and γ_{12} to the interfacial free energy. From this equation, the following observations can be made for an adhesive (1) and adherend (2) system: (i) the adhesion energy a priori increases with the surface energy of the adherend and (ii) if the surface energy of the adherend is higher than that of the adhesive (i.e. $\gamma_1 < \gamma_2$), a cohesive failure in the adhesive is expected. These predictions have not however been quantitatively confirmed experimentally, since it is well known that the measured work of adhesion is often higher than the predicted value from the thermodynamic equations [34–36].

When the adhesive is a liquid and the adherend a solid surface, the thermodynamic work of adhesion can be expressed by the following expression (Eq. (2)), known as the Dupré equation [37]:

$$W_A = \gamma_{SV} + \gamma_{LV} - \gamma_{SL} \quad (2)$$

where γ_{LV}, γ_{SV} and γ_{SL} are the surface free energies of the liquid–vapor, solid–vapor and solid–liquid interfaces, respectively. In 1805, Young [38] introduced a relationship for expressing the conditions of equilibrium at a solid–liquid interface by looking at