



Bonding of silicone rubbers on metal: (1) Chemistry of adhesion



Loïc Picard^{a,b,c}, Patricia Phalip^c, Etienne Fleury^{a,b}, François Ganachaud^{a,b,*}

^a Université de Lyon, F-69361 Lyon, France

^b INSA-Lyon, IMP, UMR5223, F-69621 Villeurbanne, France

^c Hutchinson S.A, Centre de Recherche, F-45120 Châlette-sur-Loing, France

ARTICLE INFO

Article history:

Received 13 November 2014

Received in revised form 16 January 2015

Accepted 26 February 2015

Available online 22 March 2015

Keywords:

Adhesion

Silicone elastomer

Metal

Primer

Silane

Silicone resin

ABSTRACT

The adhesion between high consistency silicone rubbers (HCR) and metal via a primer entails a complex chemistry not completely understood. This series of papers aims at defining the important criteria that govern the bonding of various HCR grades on metal surfaces. In this first study, different primer formulations were tested, thanks to a 90° peel test, showing different effectiveness toward silicone/metal attachment. Their basic components are organotitanate catalysts and a vinyltrialkoxysilane, whereas some other reactants, e.g. 3-mercaptopropyltriethoxysilane, polydimethylsiloxane chains or tetraethoxysilane, are likely introduced to bring supplementary properties to the primer film or to enhance the co-vulcanization with the silicone elastomer. From these bases, a new primer formulation, containing a silicone resin as main component, was developed successfully. However, the question of the primer selectivity for a grade of silicone elastomer still remains an issue.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

High consistency silicone rubbers (HCRs) are widely used for their intrinsic resistance properties against UV, high temperature, solvents and in a lesser extent, ozone. These elastomers are typically silica-filled PDMS linear macromolecules chemically cross-linked via organic peroxides. In the industry, the silicone rubbers are bonded with metals for the manufacturing of technical parts such as dampers, seals, etc. [1]. Strong adhesion of the silicone elastomer onto the substrate can only be obtained by covalent bonding; for metallic substrates, this is not easily obtained due to an incompatible surface chemistry [2,3].

Primer formulations for HCR are mainly quoted in the patent literature. Our group has recently written a review on the chemical adhesion of silicone elastomers on primed metal surfaces [3]. The typical composition of primer formulations for HCR generally contains between 1 and 25 wt% of a mixture of a vinyl based organosilane and organotitanate [3] in organic solvent. The advantage of this latter component lies in its dual role as coupling agent and catalyst. Commercially, primer formulations main limitation resides in the lack of information regarding the components

employed and their content. Moreover, the selectivity of a primer formulation for a type of silicone elastomer is often encountered in the industry but poorly (if not) described in the literature. Because of this matter of fact, several primer formulations should be tested before finding one that ideally works with the silicone elastomer of interest. This approach consumes a lot of time and money with no insurance of a satisfying result, which is not acceptable from an industrial point of view.

This series of papers aims at developing a primer formulation for the adhesion of high consistency silicone rubber on metals and also at bringing further understanding on the (physical) chemistries of the organosilane-based primer formulations. In this first paper, two typical primer formulations were studied to compare their chemistry with their adhesive properties on silicone elastomers of study. To do so, 90° peel tests were systematically performed. The information obtained then allowed the development of a new primer formulation containing a mixture of organosilanes and a silicone resin in an organic solvent. The second paper [4] of this series will specifically present the physical chemistry of adhesion.

2. Experimental

2.1. Materials

Two basic primer formulations, named CAP1 and CAP2 thereafter, and high damped and resilient high consistency silicone rubbers, named elastomer A and elastomer B thereafter, were

* Corresponding author at: Ingénierie des Matériaux Polymères, UMR CNRS 5223, Bâtiment Jules Verne, 17, avenue Jean Capelle, 69621 Villeurbanne, France.
Tel.: +33 4 72 43 71 04.

E-mail address: francois.ganachaud@insa-lyon.fr (F. Ganachaud).

kindly supplied by our industrial partner. Chromium (III) acetylacetonate (97%), titanium isopropoxide ($\geq 97\%$), vinyltrimethoxysilane (98%), 3-aminopropyltrimethoxysilane (98%), propylamine (98%), methylcyclohexane (99%), toluene (puriss. for GC, $>99.7\%$), tetrahydrofuran (THF, $\geq 99.5\%$) and lithium aluminum hydride (LiAlH_4 , 1.0M in THF) were purchased from Sigma–Aldrich. Xylenes ($\geq 98\%$) were purchased from Carlo Erba. Vinylated silicone resins were kindly sampled by different manufacturers. Ammonia solution (20%) was supplied from VWR Prolabo. Deuterated chloroform ($\geq 99.96\%$) was purchased from Euriso-top. Aluminum 5086/H111 plates manufactured of the 90° peel test specimens were supplied from S.A. Vannier (Pannes, France). The chemical treatments for the aluminum plates were supplied by our industrial partner.

2.2. General methods

The solid content of the primer formulations was determined by gravimetry. The nature of the catalyst in formulation CAP1 was determined by elemental analyses, which were performed by the Service Central d'Analyse, Villeurbanne (France). Nitrogen content was determined through a combustion process followed by gas chromatography detection and titanium content was obtained through a mineralization process in acid medium followed by inductively coupled plasma atomic emission spectrometry (ICP–AES) detection.

Thermogravimetry (TGA) analyses were carried out on a Q500 from TA Instrument. 25 mg of sample was heated in a platinum pan from room temperature to 900°C under a nitrogen flow (90 mL min^{-1}). The experiments were performed at a heating rate of $20^\circ\text{C min}^{-1}$.

Size exclusion chromatography (SEC) was carried out on a Malvern Viscotek GPC max equipped with two detectors (a Viscotek VE3580 differential refractometer detector and a 270 dual detector Malvern viscometer) and three Waters columns in series (300 mm length, 7.8 mm diameter, Styragel HR1, HR3 and HR4 ($5\ \mu\text{m}$ particle size)) for analysis of molar masses comprised between 100 and $600,000\text{ g mol}^{-1}$. A Shodex KF–G precolumn (10 mm length, 4.6 mm diameter and $8\ \mu\text{m}$ particle size), three Shodex columns in series (300 mm length, 8 mm diameter, KF-804 ($7\ \mu\text{m}$ particle size, porosity of $1500\ \text{\AA}$), KF-805 and KF-806 ($10\ \mu\text{m}$ particle size, porosities of 5000 and $10,000\ \text{\AA}$ respectively)) were employed for the analysis of molar masses comprised between 70,000 and $20,000,000\text{ g mol}^{-1}$. The temperature of analysis was set at 35°C both in columns and detectors. Toluene was eluted at a flow rate of 1 mL min^{-1} . The samples were prepared by dissolving materials in SEC eluent (3 mg mL^{-1}) and by filtrating the solution using a $0.2\ \mu\text{m}$ pore size filter.

The functionality and the type of silicone units (M, D, T and Q) present in the solvated primer formulations were determined by liquid state ^{29}Si NMR experiments. A second codification was employed in each family and consists at placing a superscript number corresponding to the number of oxygen atom bound to a silicon atom (e.g. Q^3 correspond to a Q unit bound to three silicon atoms). These analyses were performed on a Bruker Avance II (400 MHz), at room temperature, in 10 mm tubes and in CDCl_3 with chromium (III) acetylacetonate as a relaxation agent. The chromium complex allows getting quantitative signals.

Solid state ^{29}Si NMR analyses were performed on the solid residue which was obtained after evaporation of the primers' solvent. Solid state ^{29}Si NMR measurements were carried out on a Bruker DSX 400. A magic angle spinning probe at a rotational frequency of 10 kHz was used. A single pulse ^{29}Si excitation frequency of 79.5 MHz was employed with a pulse length of $4\ \mu\text{s}$ and a repetition of 60 s. The signal deconvolution was performed with the DMFit software.

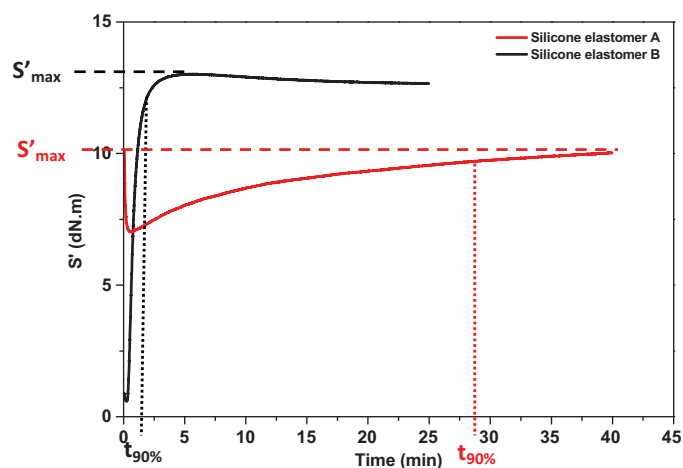


Fig. 1. Kinetic vulcanization curves for the silicone elastomers A (red line) and B (black line). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

The curing kinetics of the silicone elastomers was determined by a Moving Die Rheometer (MDR). The lower part of a heated biconical oscillating chamber applies an oscillation strain of 0.5° at 1.7 Hz and the upper part records the complex torque S^* as a function of time. For elastic materials, the elastic torque S' , corresponding to the real component of S^* ($S^* = S' + iS''$), is followed with time until it reaches a plateau value (Fig. 1).

2.3. Specific characterizations

2.3.1. Estimation of silica content in the elastomers

The percentage of residue obtained by TGA at the end of the heating ramp corresponds a priori to the quantity of inorganic fillers (i.e. silica) in the elastomer. The content of silica in the elastomer can also be estimated from the volumetric mass density of the HCR (ρ_{tot}). This theoretical mass percentage of silica was calculated using Eqs. (1)–(3) and by taking as a fair approximation a volumetric mass density of 1 for the polymer (ρ_p) (e.g. PDMS) and 2.2 for the silica [5] (ρ_s) (e.g. fumed silica).

$$\rho_{tot} = \frac{m_{tot}}{V_{tot}} = \frac{m_p + m_s}{(m_p/\rho_p) + (m_s/\rho_s)} \quad (1)$$

$$m_s = x * m_{tot} \quad (2)$$

$$m_p = (1 - x) * m_{tot} \quad (3)$$

with x , the mass percentage of silica in the HCR, which can be calculated by Eq. (4):

$$x = \frac{\rho_s * \rho_p}{(\rho_p - \rho_s) * \rho_{tot}} - \frac{\rho_s}{(\rho_p - \rho_s)} \quad (4)$$

2.3.2. Estimation of molar mass between crosslinks

Swelling measurements were performed by plunging a test sample (cylindrical disk of 6 mm diameter and 2 mm thickness, #0.15 g) of cross-linked material, having an initial dry weight (m_i), in a sealed bottle filled with 30 mL of methylcyclohexane. After 5 days, the equilibrium is considered to be reached. The sample was extracted from the bottle, gently wiped to remove the excess of solvent on the surface and immediately weighted (m_s). Three measurements were performed for each silicone elastomer. The volume fraction of swollen polymer (ϕ) was calculated according to the Eq. (5):

$$\phi = \frac{1}{1 + (m_i\rho/m_s\rho_s) - (\rho/\rho_s)} \quad (5)$$

Download English Version:

<https://daneshyari.com/en/article/7106933>

Download Persian Version:

<https://daneshyari.com/article/7106933>

[Daneshyari.com](https://daneshyari.com)