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Material behaviour

# Influence of the temperature on the mechanical behaviour of filled and unfilled silicone rubbers

T. Rey [a], G. Chagnon [a,*], J.-B. Le Cam [b], D. Favier [a]

[a] Université de Grenoble, Laboratoire 3SR, Domaine Universitaire, BP53, 38041 Grenoble Cedex 9, France
[b] Université de Rennes 1, L.A.R.M.A.U.R. – CNRS 6274, Campus de Beaulieu, Bât. 10B, 35042 Rennes Cedex, France

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ABSTRACT

This paper investigates the effects of temperature on the mechanical properties of silicone rubbers. First, differential scanning calorimetry tests are performed to determine the crystallization and melting temperatures. Second, mechanical tests are carried out at different temperatures above that of crystallization, up to 150 °C. In this temperature range, the silicone rubbers exhibit entropic behaviour. The neo-hookean model is used to fit the mechanical response. Third, the effects of temperature on the hysteresis, the stress softening and the stress relaxation are studied. Strong differences are observed and discussed.


## 1. Introduction

Silicone rubbers are increasingly used in many applications that differ in nature, for instance automotive applications, food storage products, footwear, electronics. This is mainly explained by their easiness of cure and, more generally, of manufacture. Moreover, silicone rubbers do not react with most chemicals, which explains why they are used in many medical applications.

Classically, silicone rubbers are filled with mineral fillers such as silica in order to increase their stiffness. In this case, fillers greatly complicate the mechanical response by inducing numerous phenomena: non-exhaustively, stress softening [1], the Payne effect [2,3] and mechanical hysteresis. Even although mechanical response of filled and unfilled silicone rubbers has already been characterized in the literature at room temperature [4–6], no study investigates the effects of temperature on the mechanical response, while the large variety of applications requires a large range of service temperatures. Moreover, temperature variation affects the interaction between the fillers and the rubber matrix [7] and, consequently, it is necessary to study both filled and unfilled silicone rubbers.

This paper aims, therefore, at investigating the influence of temperature above that of crystallization on hyperelasticity, stress softening, mechanical hysteresis and stress relaxation. Section 2 presents the materials and the experimental setup. Section 3 gives the results obtained for both materials. The evolution of the various phenomena involved in the deformation of silicone rubbers is discussed in Section 4. Finally, concluding remarks close the paper.

## 2. Experimental setup

This section focuses first on the preparation of the two studied silicone rubbers (Bluestar RTV 141 and RTV 3428), second on the identification of their characteristic temperatures, and third on the mechanical tests performed.

### 2.1. Preparation of the silicone rubbers

The preparation process was similar for the two materials. The first step consisted of blending two liquid

* Corresponding author. Tel.: +33 4 76 82 70 85; fax: +33 4 76 82 70 43.
*E-mail addresses:* gregory.chagnon@grenoble-inp.fr, gregory.chagnon@wanadoo.fr (G. Chagnon).

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components, the uncured unfilled silicone RTV 141A (or RTV 3428A for the filled silicone) and 10/1 phr in weight of the curing agent RTV 141B for the unfilled silicone (or RTV 3428B for the filled silicone). The mixture was then degassed for 30 min in a vacuum chamber to remove any air bubbles to ensure the material homogeneity. The degassed liquid was injected by means of a medical syringe into a closed mold to guarantee a constant specimen thickness (2 mm). Finally, the mold was put in an oven at a temperature of 70 °C for 4 h to cure the material. This procedure was previously used for the unfilled [4] and filled [5,6] silicone rubbers for studying their mechanical properties at room temperature.

Before testing the temperature effects on the mechanical properties, it is necessary to check that the material is fully cross-linked in order to not superimpose temperature and cross-linking effects. To this end, the materials were heated at different temperatures for different times after curing and then cooled at room temperature. One day rest was imposed before performing the mechanical tests. For each specimen, a uniaxial tensile test was carried out at room temperature. Fig. 1 presents the results obtained for the unfilled silicone in terms of the nominal stress versus the stretch ratio λ (defined as the ratio between current and initial lengths). As shown in this figure, the material prepared with the supplier recommendations (4 h at 70 °C) is not fully cross-linked. Indeed, the specimens heated at 150 °C for 3 and 6 h exhibit stiffer behaviour. Moreover, no variation in stiffness is observed after a heating at 150 °C for 3 h. The microstructure of the material is, therefore, stabilized after such a thermal treatment. Consequently, in the present study, the material was heated 3 h more at 150 °C. This new procedure ensures that the change in the mechanical response during the test in not due to an increase in cross-linking.

It should be noted that no difference was observed for the filled silicone whatever the applied thermal treatment, meaning that the recommendations of the supplier, *i.e.* 4 h at 70 °C, lead to a stabilized microstructure.

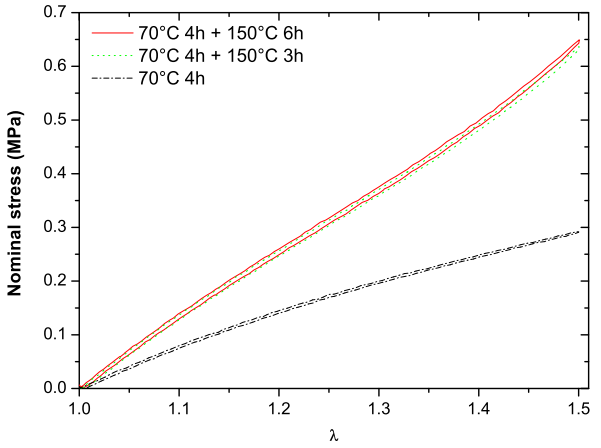


**Fig. 1.** Influence of curing time on the strain-stress relationship for the unfilled RTV 141 silicone.

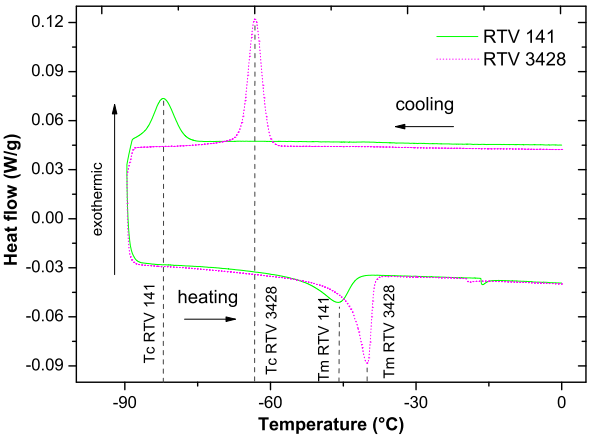


**Fig. 2.** Heat flow versus temperature measured by means of a DSC for an unfilled and a filled silicone for a temperature cycle from 0 °C to −90 °C and from −90 °C to 0 °C. Tc and Tm are the temperatures where crystallization and crystallites melting occur, respectively.

### 2.2. DSC and DMTA analyses

DSC (Differential Scanning Calorimetry) and DMTA (Dynamic Mechanical and Thermal Analysis) tests were carried out to define the characteristic temperatures of the two silicones, *i.e.* temperatures of crystallization and melting for a given temperature rate.

The DSC was performed with a TA Q200 differential scanning calorimeter. The cooling rate was set to 2 °C per minute, and the temperature range between 0 °C and −90 °C. Then, heating took place between −90 °C and 0 °C with the same heating rate as previously used. Specimens of 29 and 37 mg weight were used for the unfilled and filled silicones, respectively. Results are presented in Fig. 2. As shown in this figure, an exothermal peak in the heat flow-temperature curve is observed for the two materials during cooling, this corresponds to the crystallization of some of the polymer chains. During heating, an endothermal peak is observed, which corresponds to the crystallites melting. The temperatures for which crystallization and crystallites melting occur are denoted respectively Tc and Tm in the following. The values of these characteristic temperatures are reported in Table 1. These tests do not allow us to determine the glass transition temperature for both materials, which occurs at temperature lower than −90 °C.

Dynamic Mechanical Thermal Analysis (DMTA) tests were carried out by means of a Gabo Eplexor 500N machine with load cell capacity of 25 N. This type of test is classically used to study the amplitude dependence of filler-reinforced rubbers (see for instance [8]). The test consists firstly in cooling with a temperature range between 150 °C

**Table 1**
Characteristic temperatures for the two silicone rubbers.

| | Crystallization temperature | Melting temperature |
|---|---|---|
| RTV 141 | −83 °C | −47 °C |
| RTV 3428 | −66 °C | −41 °C |