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The influence of static pre-stretching on the mechanical ageing of filled silicone rubbers for dielectric elastomer applications

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ABSTRACT

Dielectric elastomer (DE) pre-stretching is a key aspect of attaining better actuation performance, as it helps prevent electromechanical instability (EMI) and usually lowers the Young's modulus, thus leading to easier deformation. The pre-stretched DE is not only susceptible to a high risk of tearing and the formation of mechanical defects, but films with sustained and substantial strain may also experience mechanical degradation. In this study a long-term mechanical reliability study of DE is performed. Young's moduli, dielectric breakdown strengths and dielectric permittivities of commercial silica-reinforced silicone elastomers, with and without an additional 35% (35 phr) of titanium dioxide (TiO_2), were investigated after being subjected to pre-stretching for various timespans at pre-stretches to strains of 60 and 120%, respectively. The study shows that mechanical stability when pre-stretching is difficult to achieve with highly filled elastomers. However, despite the negative outlook for metal oxide-filled silicone elastomers, the study paves the way for reliable dielectric elastomers by indicating that simply post-curing silicone elastomers before use may increase reliability.

1. Introduction

The reliability of dielectric elastomer (DE) transducers depends on the types of material used, as well as fabrication techniques and design and transducer operating conditions (such as maximum stretching, applied frequency and amplitude of the applied voltage). The acrylic double-adhesive VHB 4910, produced by 3 M, is one of the best-performing elastomers with respect to actuation strain (s) at a given applied field, and it chiefly outperforms silicone-based elastomers over short time scales. Silicone elastomers, however, possess a faster actuation response as well as reliability over time, since performance remains more or less unaltered up to about 10 million cycles when pre-stretching is avoided [1]. Pre-stretching is well-known to be a prerequisite for the actuation of acrylic-based elastomers, since it simultaneously reduces thickness, decreases the Young's modulus and suppresses electromechanical instability (EMI). [2–4] The effect of the first two parameters can be seen from the equation of actuation derived by Pelrine et al. [3]:

$$s = -\epsilon_r \epsilon_0 \frac{(V/d)^2}{Y} \tag{1}$$

where s is actuation strain, V is applied voltage, d is the thickness of the film and Y is the Young's modulus.

Pre-stretching has also been shown to cause the alignment of elastomer chains in the plane of stretching [5]. This alignment, which is perpendicular to the direction of the electric field, leads to an increase in breakdown strength, because charge carrier movement is impeded. [6]. For acrylics, pre-stretching is also favourable due to strain-softening, whereas for silicone elastomers the elastomer usually does not show the same tendency and in many cases strain-hardening behaviour actually sets in. However, pre-stretching remains very favourable for silicone elastomers, as largely improved actuation strains can be obtained through the avoidance of EMI.

The most common failure modes of DE transducers are pull-in instability, dielectrical breakdown and material strength failure [7,8]. Electromechanical pull-in instability, also known as electromechanical instability (EMI), was identified by Stark and Garton [9] and occurs when Maxwell pressure locally exceeds the com-

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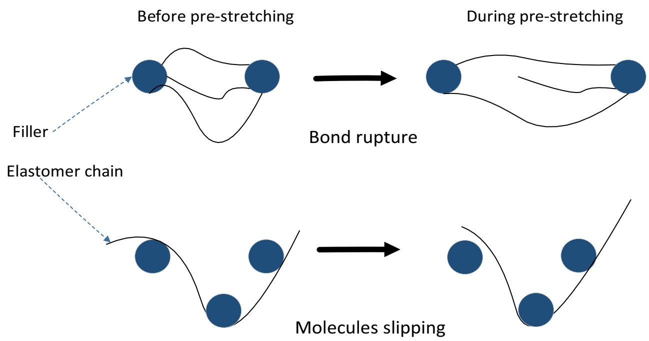

Fig. 1. Physical explanations of the Mullins effect.

pressive stress of the elastomer [4–10]. For silicone elastomers, mechanical strength failure is very seldom a failure mode, due to the ultimate extensibility of silicone elastomers usually exceeding 300%. Common actuation strains introduced in silicone elastomers are of the order of 20%, so even with pre-stretching the overall strain is far below their maximum extensibility. For silicone elastomers to make the very most of their potential, i.e. approach actuation strains of the order of their maximum extensibility, greater energy – and thus permittivity – is required.

The major disadvantage of silicone elastomers over acrylics is their low dielectric permittivity. Several approaches have been developed to enhance dielectric permittivity, with the addition of metal oxides being the most frequently investigated due the ease of elastomer formulation. TiO_2–silicone composites have by far been the most commonly investigated elastomer system due to the availability of nanosized TiO_2 particles with various surface functionalizations. More complex approaches exist such as the covalent grafting of dipoles [11–13] and the creation of heterogeneous elastomers with hard and soft domains from controlled network formation [14–17]. Incorporating rigid fillers, such as titanium dioxide, into the cross-linked PDMS matrix increases the dielectric permittivity of the resulting composite elastomer. Mechanical properties are also affected, with results varying according to particle size and surface treatment, from reinforcing to softening [18–22]. On the other hand, a thinly filled elastic film that maintains high strain for a given period of time will, to some extent, suffer mechanical ageing at the microscopic level. The Payne and Mullins effects explain hysteresis in the mechanical properties of filled elastomers. The Payne effect refers to the effect of the strain dependence of the dynamic viscoelastic properties of filled elastomers above their glass transition temperature [23]. Clement et al. [24] investigated the Payne effect in SiO_2-filled PDMS elastomers, and they posited it as the existence of a gradient in elastomeric chain mobility from the PDMS filler interface to the bulk, leading to a stress-softening effect at low strains upon “initial activation” of the elastomer. Clement et al. [25] also investigated the Mullins effect, i.e. the stress-softening phenomenon that occurs in elastomers during the first deformation of a given strain [26]. They attributed Mullins softening to bond ruptures or elastomer chain slippage (as illustrated in Fig. 1). Additionally, they observed the dependency of the Mullins effect on the degree of filler dispersion. They found that non-homogeneity in the spatial distribution of SiO_2 inside the elastomer matrix exhibits a greater Mullins effect due to the fact that larger local strains were acquired in regions with high concentrations of SiO_2. Due to its disruptive nature, stress softening has often been considered as damaging, but it does not necessarily lead to failure [27]; in general, it just leads to strain-history-dependent mechanical properties, though this dependency can be avoided by stretching the elastomer to more than its maximum actuation strain before applying it in products. Irradiation ageing has previously been studied by Stevenson et al. [28], but during such experiments crosslinking density changed, whereas in this study crosslink density remains constant.

Generally, silicone elastomers are commercially synthesised through the equilibration polymerisation of cyclic oligomers and end groups in the presence of acid or basic catalysts [29]. One of the disadvantages of this process is the production of by-products as a result of the reaction, consisting of unreacted cyclic oligomers [30]. These residues are mobile within the silicone, and they can also migrate to a device interface. This migration during post-manufacture changes the elastomer surface as well as its mechanical properties such as tensile strength, tear strength, maximum elongation, etc [31]. As reported by Brook et al. [32], these volatile siloxanes from commercial silicones usually remain within the elastomer when post-curing has been omitted. Post-curing is usually conducted by heating the elastomer far above its curing temperature but below its degradation temperature for some time. Brook et al. [32] showed that the mechanical properties of the elastomer were enhanced (a larger Young’s modulus, greater tensile strength and lower maximum extensibility) upon post-curing. In this case, post-curing was performed by heating a cured elastomer at 200 °C for 4 h subsequent to the traditional curing procedure, where the most common conditions for dielectric silicone elastomers are curing at ∼120 °C for 10–30 min [33]. To our knowledge the effect of post-curing on, for example, dielectric breakdown strength has never been investigated, since the fraction of volatiles is so low (usually cited at 1–2% by the elastomer supplier) that it seems irrelevant.

In order to introduce reliable DE-based products, the pre-stretching frame should be designed in such a way as to impart uniform pre-stretching to the elastomer film over a large area, regardless of whether it is a symmetrical or non-symmetrical pre-stretch [7]. There is a high risk of tearing at the corners of the grips used to hold the thin polymeric film in the pre-stretch equipment, which would lead to premature material strength failure, as the thin films are prone to tearing [7]. With respect to the elastomers, precautions are also required. Micro-voids, deviations in film thickness, surface roughness, inhomogeneous mechanical stiffness, dust particles, contaminants and scratches are the most common defects in thin elastomer films. For acrylics it was shown that during mechanical tests, additional groove-like defects rapidly appear at the film edges attached to rigid supports, and they expand gradually as the test continues [7]. The propagation of such cracks/grooves at stress gradients will age the material faster, thereby leading ultimately to mechanical failure.

As reported by Meunier et al. [34], unfilled PDMS lacks the Mullins effect, hysteresis and strain rate dependency. However, for DE applications filled, reinforced silicones are required to obtain acceptable performance. This study was performed in order to understand the intrinsic mechanical behaviour of pre-stretched PDMS elastomers, with and without additional permittivity enhancing fillers, over time. Furthermore, the study aims at elaborating how mechanical ageing affects other parameters relevant to the DE being used, namely the Young’s modulus, electrical breakdown strength and dielectric permittivity.

2. Methodology

2.1. Materials

Four different compositions from two commercial silicone elastomers, without and with one type of permittivity enhancing filler (TiO_2), were investigated. The elastomers were Elastosil® LR 3043/30 A/B and ELASTOSIL® RT® 625 A/B. POWERSIL® LR® 3043/30 A/B is a high-viscosity LSR and is supplied as a two-part system. The mixing ratio of parts A and B is 1:1. ELASTOSIL® RT®