



HAL
open science

Electroactive soft polyurethanes used as a smart rubbers

M. H. Jomaa, J. -Y. Cavaille, L. Lebrun, L. Seveyrat, K. Masenelli-Varlot

► To cite this version:

M. H. Jomaa, J. -Y. Cavaille, L. Lebrun, L. Seveyrat, K. Masenelli-Varlot. Electroactive soft polyurethanes used as a smart rubbers. 8th European Conference on Constitutive Models for Rubbers (ECCMR), Jun 2013, San Sebastian, Spain. pp.693-696, 10.1201/b14964-128 . hal-01814443

HAL Id: hal-01814443

<https://hal.science/hal-01814443>

Submitted on 24 Jan 2022

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution - NonCommercial 4.0 International License

Electroactive soft polyurethanes used as a smart rubbers

M.H. Jomaa

*MATerials EngIneering and Science (MATEIS), INSA Lyon, CNRS-UMR 5510, Villeurbanne, France
Laboratoire de Génie Electrique et Ferroélectricité, LGEF EA682 INSA Lyon, Villeurbanne, France*

J.-Y. Cavaillé

MATerials EngIneering and Science (MATEIS), INSA Lyon, CNRS-UMR 5510, Villeurbanne, France

L. Lebrun & L. Seveyrat

Laboratoire de Génie Electrique et Ferroélectricité, LGEF EA682 INSA Lyon, Villeurbanne, France

K. Masenelli-Varlot

MATerials EngIneering and Science (MATEIS), INSA Lyon, CNRS-UMR 5510, Villeurbanne, France

ABSTRACT: Some polyurethanes have demonstrated their ability to convert electrical energy into mechanical energy and vice versa. Furthermore, these materials are lightweight, very flexible, presenting low manufacturing costs, and can be readily molded into any desirable shape. It has been recently pointed out that this strong electrostriction results mainly from the phase separation into domains rich in Hard Segments (HS) with high dielectric constant and domains rich in Soft Segments (SS), and weak dielectric constant. This, in turn leads to heterogeneities of both elastic constants and dielectric constants and to electric field gradients, which shrinks the soft domains and compresses the whole material. It is thus important to optimize the polyurethane microstructure, which mainly depends on the polymer composition. In this work, we compare three types of commercial PU, namely PU88, for Estane 58888 NAT 021, PU75, for Estane X-4977 NAT 039 and PU60 for Estane ETE60DT3 NAT 022 with different weight fractions of (HS) and (SS): (45%, 55%), (26%, 74%) and (65%, 35%), respectively. In order to select the best PU for its use as actuator or energy harvesting material, a complete analysis of the physical properties (namely electrical, mechanical and electrostrictive) of these 3 pure PUs was performed.

1 GENERAL INSTRUCTIONS

Electroactive Polymers (EAPs), whose responses are stimulated by external electrical fields, have drawn tremendous attention in recent years. These EAPs have the capability to change their size due to the electrostrictive and Maxwell effects which are a quadratic function of the applied electric field. Even if the electromechanical coupling is relatively weak for polymers, they can generate high strains. Among the various EAPs, polyurethane (PU) elastomers are of great interest due to the significant electrical-field strains [2], [3], and due to their attractive and useful properties; such as flexibility, light weight, high mechanical strength and easy processing to large area films as well as their ability to be molded into various shapes [4].

From a theoretical point of view, the total strain is a combination of electrostriction and Maxwell strains, as shown in Equation (1) [5]:

$$S = S_{\text{electrostriction}} + S_{\text{Maxwell}} = M_{33}^* E^2 \quad (1)$$

The Maxwell stress effect comes from the interaction between electrical charges in the electrodes which result in electrostatic attractions between the electrodes. The strain S_{Maxwell} corresponds to the equilibrium between electrostatic stress and the mechanical response of the dielectric material, and as a consequence a thickness contraction of the polymer is observed:

$$S_{\text{Maxwell}} = -\frac{\epsilon_r' \epsilon_0}{Y} E^2 \quad (2)$$

where, ϵ_r , ϵ_0 refer to the dielectric constant of the polymer and to vacuum permittivity, respectively.

The electrostriction is the change in dimensions of a dielectric material occurring as an elastic strain when an electric field is applied. It is the direct coupling between the polarization and

mechanical response in the material. By assuming a linear relationship between the polarization P and the electrical field E , $S_{electrostriction}$ can be expressed by Equation (3):

$$S_{electrostriction} = QP^2 = Q\epsilon_0^2 (\epsilon_r' - 1)^2 E^2 \quad (3)$$

where, Q is the electrostrictive coefficient.

If the deformations due to the Maxwell stress effect account for a negligible part of the total strain, it has been previously published [6] that the M_{33} coefficient of electrostriction varies like $(\epsilon_0 (\epsilon_r' - 1)^2)(\epsilon_r' Y)$.

As seen in these relations, actuation capabilities depend on the dielectric and mechanical properties of the polymer. It has been recently pointed out that this strong electrostriction results mainly from heterogeneities in contrast of both elastic constants and dielectric constants and to electric field gradients, which shrink the soft domains and compress the whole material [1]. These heterogeneities in polyurethanes result from the phase separation into domains rich in Hard Segments (HS) with high dielectric constant and domains rich in Soft Segments (SS), and weak dielectric constant.

In order to better understand electrostriction effect in polyurethane films and to choose the more appropriate PU for actuations and harvesting energy, a complete study was performed.

This paper deals with the influence of weight fraction of (HS) on physical properties of 3 different PU elastomers. The dielectric and viscoelastic properties are presented and discussed. Finally measurements of the thickness strain under an applied electrical field are shown for the 3 PU. In conclusion the choice of the best PU is discussed on the basis of specific requirements of electrostriction and actuation.

2 EXPERIMENTAL SECTION

Polyurethanes Elastomers are generally co-block polymers with two major blocks; namely the hard and soft segments. The Hard Segment (HS) is composed of 4,4' methylene bis (phenyl isocyanate) (MDI) and 1,4-butanediol (BDO). Often, poly(tetramethylene oxide) is used as soft segments (SSs). The three different types of PU, are commercially available and were provided by the same company, Lubrizol, namely PU88, PU75 and PU60 with different weight fractions of (HS) and (SS), and with different molecular weight of SSs; 1000 (g/mol) for PU88, PU60 and 2000 (g/mol) for PU75. They are synthesized by the same industrial process from the same initial chemical components. The properties of the three types of PU are summarized in Table 1.

Table 1. Main physical properties of the three PU.

	PU88	PU75	PU60
Tg (K)	228	206	254
Hardness (shore)	88A	75A	60D
HS (%wt)	45	26	65
SS (%wt)	55	74	35
Density (g/cm ³)	1.13	1.07	1.17

The polymer films were prepared by following a solution casting method. Before use, the PU granules were heated at 80 °C for 3 h. Then they dissolved put in N,N-dimethylformamide (DMF, Sigma-Aldrich D158550, 99%) with a ratio of 25% weight volume PU into DMF. The solution was heated at 80 °C for 8 hour under mechanical agitation, until a homogeneous and viscous solution was obtained. The solution is then kept overnight to let it remove air bubbles. Afterwards, this solution was cast on glass plates with an Elcometer 3700 doctor blade film applicator, put in an oven at 60°C for one day, then removed from glass. A second heating treatment at a temperature below the melting temperature of hard segment was performed in order to eliminate the residual solvent. The thickness of the films was about 100 μm after drying. The elaboration condition was optimized for the 3 PU.

The dielectric properties of these films were measured with a Schlumberger Solartron 1296 dielectric interface and 1255 impedance analyzer. Both surfaces of the film were coated with a gold electrode of 20 mm of diameter, deposited by sputtering (Cressington 208 HR). An AC voltage of 1 Vrms (DC voltage was null) was applied on the polymer films positioned between two circular electrodes at room temperature, over a frequency range of 10⁻¹ to 10⁵ Hz. Thus, complex conductivity as well as complex dielectric constants ϵ^* for the different samples were displayed and a special care was taken on the dielectric losses through $\tan\delta$ of imaginary component divided by real component of ϵ^* .

Viscoelastic properties of the 3 PU were performed using a Dynamic Mechanical Analysis (DMA) working in torsional mode. The samples were shaped as rectangular, with a length of 12 mm, a width of ~3 mm, for 100 μm of thickness. All measurements were performed as a function of temperature (isochronal measurements) at $F = 1$ Hz with a heating rate of 1 K/min over a temperature range from 180 to 350 K.

The field-induced thickness strain S was measured on circulars sample (25 mm of diameter) with a homemade setup based on a double-beam laser interferometer measurement (Agilent 10889B) [7]. Uncoated samples were positioned between two circular electrodes. A mirror is placed on the upper

electrode to reflect the laser beam. A bipolar electric field (0.1 Hz) is supplied by a function generator (Agilent 33250A) amplified by a factor 1000 through a high-voltage lock-in amplifier (Trek10/10B). Measurements were made at room temperature on samples of 100 μm thickness.

3 RESULTS AND DISCUSSION

3.1 Dielectric properties

3.1.1 Real conductivity

Figure 1 presents the real electrical conductivity in function of the frequency for the 3 PUs. In all samples, two frequency regions can be observed: one for which the conductivity is almost constant (frequencies lower than 10 Hz) and which is attributed to electrical charge motion and the other one (frequencies higher than 10 Hz) where the conductivity is proportional to the frequency and corresponds to the classical dielectric behavior [8]. By increasing the weigh fraction of (HS), the DC conductivity decreases at low frequency but slightly increases at high frequency, which corresponds to a higher dielectric constant. DC conductivity is responsible of electrical losses (Joule effect).

Table 2, summarizes the main dielectric properties of the 3 PU at low frequency (0,1 Hz). The real part of the dielectric constant is almost the same between the 3 PU, and thus is independent of the weight fraction of (HS). However the dielectric loss and the conductivity decrease at increasing of the content of (HS). This can be explained by decreasing of ionic mobility and/or impurity in hard polyurethane at low frequency.

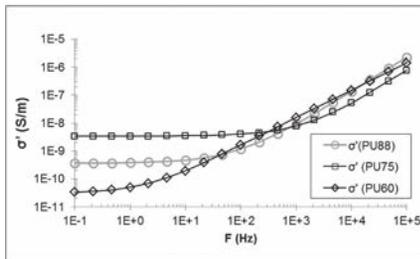


Figure 1. Real electric conductivity of 3 PUs at room temperature.

Table 2. Dielectric properties of the 3 PUs at 0.1 Hz.

	PU88	PU75	PU60
$\epsilon' r$	9.1	9	7.6
$\tan \delta$	8	73	0.9
$\sigma' (S/m)$	$3.7 \cdot 10^{-10}$	$3.3 \cdot 10^{-9}$	$3.4 \cdot 10^{-11}$

3.2 Mechanical properties

3.2.1 Visco-elastic properties

Visco-elastic properties of the 3 PU were determined with the help of DMA, which is a useful technique to study polymer relaxations. It allows measuring the elastic shear modulus G , and the dissipation factor $\tan \phi$ which is a probe of the molecular mobility.

Figure 2 shows shear modulus on left axis and mechanical loss on the right axis of the 3 PU versus temperature. The glass transition temperature (T_g) roughly determined from DMA was very close to the DSC (Differential Scanning Calorimetry) data. It is worthy to notice that the increase of G_{at} increasing temperature for PU75 corresponds to its partial crystallization during the experiment. The $\tan \phi$ peak in the glass transition temperature range gives us more details about the morphology. The composition of the PU greatly affects the T_g of SSs. Furthermore the shape of the peak also changes, which could be attributed to microstructures with different phase mixings.

For instance, according to dynamic mechanical measurements displayed in Figure 2, PU88 has almost constant shear modulus and low mechanical loss around room temperature, and a large temperature of utilization range. PU60 have high mechanical loss and variable shear modulus at room temperature. Moreover PU75 exhibits one peak and a shoulder: the peak is related to the glass transition relaxation and the shoulder corresponds to the crystallization of (SS), which has been confirmed by DSC measurements.

3.3 Electrostriction

When films are submitted to electric field variations (triangular potential at 0.1 Hz) perpendicular to their main surfaces (Z axis), it is possible to detect thickness variations using an interferometer. Thus relative thickness deformation S was measured along the Z axis, normal to the main surfaces of the sample.

Figure 3 reveals electromechanical activities of the 3 PUs as a function of square of applied electric field E^2 . The electromechanical behavior of the PU is being electrostrictive in nature and exhibit a quadratic strain versus electric field, according to Eq. (1). It is worth noticing that the thickness strain is negative, which indicates a compression of the film. Depending on the electric field magnitude E , two distinct strain behaviors can be defined, regardless of the weight fraction of HSs: (i) a quadratic behavior in the low electric field region, where S increases linearly with E^2 , according to Eq. (3), and (ii) an asymptotic behavior, where S remains about constant in the high applied field region up to electrical breakdown. Up

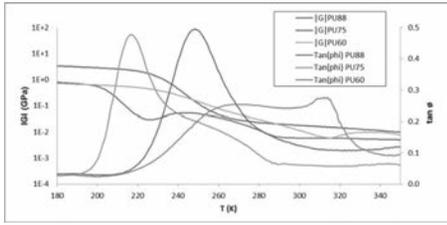


Figure 2. Typical DMA spectrum of 3PU polyurethane sample.

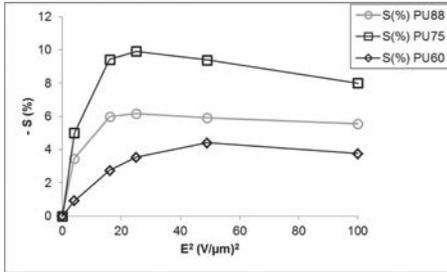


Figure 3. Evolution of the strain amplitude in function of the square of the electric field amplitude.

to now, no physical modeling of this latter effect has been proposed in the literature.

With an electric field $E = 4$ (V/μm), PU75 has the highest maximum deformation (9.43%), followed by PU88 (5.97%) and PU60 (2.75%). These results are consistent with an increase of their Young's modulus in the experimental temperature range, which makes the deformation more difficult.

4 CONCLUSIONS

Three PUs, with similar compositions but with different fractions of HS, have been characterized to better understand electrostriction and to choose the best composition for actuations and energy harvesting. The study included the characterisation of the electrical, mechanical and electrostrictive properties.

It was found that PU88 has a T_g at 228 K and an average Young's modulus of about 30 MPa, with low mechanical losses at room temperature. In addition, its modulus remains about constant around room temperature. PU88 has also a large dielectric constant, and relatively good electrostrictive properties (6 μm with 4 V/μm, $M_{33}=8.6 \cdot 10^{-15}(\text{m/V})^2$). PU75 is more flexible with a low Young's modulus (15 MPa at room temperature), with significant mechanical and electrical losses. It is more conductive than the two other PUs.

Moreover, the modulus varies significantly around room temperature. PU75 exhibits also the best deformation, since it is able to deform until 10 μm at 4 V/μm $M_{33}=12.5 \cdot 10^{-15}(\text{m/V})^2$. Finally, PU60 has the higher stiffness with a Young's modulus around 150 MPa with small mechanical and electrical loss, their T_g is around 254 K.

For actuation and energy harvesting applications, an intense electrostriction is sought but the device has to be stable over the largest range of temperature around room temperature. Because of the significant losses observed for PU75, a better compromise is most probably PU88.

ACKNOWLEDGEMENTS

The author acknowledges the financial support of the French Agence Nationale de la Recherche (ANR), under grant NAPOLECO (ANR-2010-INTB-910-01).

REFERENCES

- Gildas Diguët, Agnes Bogner, Jean-Marc Chenal & Jean-Yves Cavaille. 2012. Physical modeling of the electromechanical behavior of polar heterogeneous polymers. *Journal of Applied Physics* 112(114905): 1–8.
- Masashi. Watanabe, Toshihio. Hirai, Makoto. Suzuki & Amaike Yoichi. 1999. Electric conduction in bending electrostriction of polyurethanes. *Appl. Phys. Lett.*, **18**: 2717–2719.
- B. Guiffard, L.S., G. Sebald and D. Guyomar, Enhanced electric field induced strain in non percolative carbon nanopowder/polyurethane composites. *J. of Phys. D: Appl. Phys.*, (2006). **39**, 3053.
- C. Putson, Laurent. Lebrun., Daniel Guyomar, N. Muensit, Pierre-Jean Cottinet, Laurence Seveyart & Benoit Guiffard. 2011. Effects of copper filler sizes on the dielectric properties and the energy harvesting capability of nonpercolated polyurethane composites *Journal of Applied Physics* **109** 024104.
- Zhang Qiming M, Su, J, Kim Chy Hyung, Ting Robert Ert & Capps, Rodger. 1997. An experimental investigation of electromechanical responses in a polyurethane elastomer. *Journal of Applied Physics*. 81, 2770–2776.
- Francois Megatech Guillot & E. BalizerJ. 2003. Electrostrictive effect in polyurethanes. *Journal of Applied Polymer Sciences*. **89**, 399.
- Komkrisd Wongtimnoi, Benoit Guiffard, Agnes. Bogner-Van de Moortèle, Laurence. Seveyart, C. Gauthier & Jean-Yves. Cavaille. 2011. Improvement of electrostrictive properties of a polyether-based polyurethane elastomer filled with conductive carbon black. *Composites Sciences and Technology*. **71**.885–892.
- Jeppe C. Dyre & Thomas B. Schröder. 2000. Universality of AC Conduction in Disordered Solids. *Reviews of Modern Physics*. **72**.873–892.