Origin of Large Field-Induced Strain of Azobenzene/Polyurethane Blend Dielectric Elastomers

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ABSTRACT: Herein a diaphragm type dielectric elastomer actuator by blending azobenzene dyes into polyurethane matrix (Azo/PU) is described. The effects of azobenzene content on dielectric, mechanical, electromechanical properties of the Azo/PU blends are discussed. The resultant blends with azobenzene content ranging from 1 to 8wt% were characterized. The dielectric permittivity of PU increased from 8.0 to 11.1 (increasing of 38.5%) at 1wt% Azo content and reached a maximum of 35.6 (increasing of 343%) at 4wt% Azo content. By blending with small content of Azo the dielectric breakdown strength reached 57kV/mm, which is 86% higher than that of the neat PU. The 30 µm thick diaphragm of Azo/PU blend with 1wt% Azo content exhibited the highest actuated displacement at the center around 700 µm. Meanwhile the neat PU gave a displacement of 25 µm. That is a 26-fold increase in actuation obtains by blending with only 1wt% Azo dyes into the PU matrix. Infrared spectroscopy was used to characterize the structure of the Azo/PU blends. The particular
chemical structure Azo/PU blend containing 1wt% of Azo dyes is proposed to be responsible for the improvement in electromechanical actuation.

Keywords: Dielectric elastomer actuator, Diaphragm, Electromechanical Actuation, Polyurethane, Azobenzene

1 Introduction

During past two decades, materials with high permittivity (high-\( k \)) as the key component in the emerging field of flexible and stretchable electronics have received increasing interests.\(^1\) Specially high-\( k \) soft matters have shown a rapid expansion for wearable electronic devices\(^5,6\), micro-electromechanical systems (MEMS)\(^7,9\) and many others.\(^10-12\) Dielectric Elastomer Actuators (DEAs) are insulating soft dielectrics that could exhibit considerable strain and/or stress when subjected to an external electric field.\(^10\) Intensive attention has been devoted to this field since the pioneer work of Pelrine et al who have reported a DEA with actuation greater than 30% in thickness and 100% in area.\(^13,14\) Due to the similarity of motion, DEA has been proposed as artificial muscles which has been found applications in many fields such as valves and pumps\(^15,16\), loudspeakers,\(^17\) displays\(^18,19\), energy harvester\(^5,20\) or biomimetism technologies.\(^21\) However, the fabrication of advanced elastomeric materials for ideal DEAs use is still a great challenge. Pelrine\(^13\) has demonstrated that a DEA could be compared to a stretchable plate capacitor and deduced the Maxwell stress occurring in the dielectrics during actuation, which can be expressed as:

\[
\sigma = \varepsilon \varepsilon_0 E^2 \quad (1)
\]

where \(\varepsilon\) is the relative permittivity of the dielectric material, \(\varepsilon_0\) is the free permittivity of vacuum (8.85x10\(^{-12}\) F.m\(^{-1}\)) and \(E\) is the electric field. This relation is valid for low stress and strain in a DEA. Thus particular attention has been paid to find a model to describe a DEA at high deformation. In this objective hyperelastic models have been used. Neo-Hookean and
Mooney-Rivlin models are widely used in industry but these models can’t be used for local value of strain over 200%.\textsuperscript{[22]} To describe high strain of DEA, new models that recovered at particular condition one or both the previous models cited, are used such as Arruda&Boyce and Ogden models.\textsuperscript{[23]}

Furthermore many theoretical works flourished in order to predict the performance and understand the mechanism of actuation.\textsuperscript{[24,25]} From the point of view of material design, literature shown that the strategy to improve the electromechanical actuation performance of DEAs should be enhancing the dielectric permittivity and decreasing the elastic modulus simultaneously while keeping a high breakdown strength.\textsuperscript{[26,27]} In this case the actuation sensitivity is defined as:

$$\beta = \frac{\varepsilon}{\gamma} \quad (2)$$

This actuation sensitivity is often used as a figure of merit to describe a theoretical improvement for actuation abilities.\textsuperscript{[28,29]}

Commercial low-cost elastomers such as acrylates (3M VHB)\textsuperscript{[30]}, silicone rubbers\textsuperscript{[12]}, and natural rubbers\textsuperscript{[31]} has been widely investigated and demonstrated actuation abilities.\textsuperscript{[32-34]} Till now, the performances of artificial muscles based on DEA have already overpassed those of natural muscles.\textsuperscript{[35]} However, the high electric field (>50kV/mm) needed to achieve satisfied actuation is limiting their commercial development. Over the past decade, large efforts have been devoted to lowering the actuation electric field of DEAs. An electric field of 20kV/mm is considered as unharmsful electric field for biomedical devices\textsuperscript{[15,17-19]} and human-machine interface.\textsuperscript{[36]} Several strategies were employed to improve the actuation sensitivity of DEAs. The introduction of organic or inorganic filler with high dielectric constant into the polymer matrix is the most common method to increase the permittivity but generally increase the stiffness of the material, which compromises the effect of filler addition.\textsuperscript{[37-41]} Another
approach is blending the elastomer with a plasticizer to reduce the stiffness.\textsuperscript{41,42} Both approaches could partially improve the electromechanical actuation of resultant elastomer but still stand far from the ideal DEAs. The use of liquid crystal or ionic structures for electromechanical actuation began to appear few years ago.\textsuperscript{43,44} But more material systems are needed to be exploited to fully understand the physics behind the electromechanical actuation and develop better elastomer candidates for practical DEA applications. Nevertheless, it has been recently highlight that the microstructure of materials could greatly influence the electromechanical actuation results.\textsuperscript{45} Such structure impact on electrostrictive DEA has been seen and some studies point out that the electrostriction may stabilize the DEA during the snap-through instability,\textsuperscript{46,47} a common mode of failure that limited the actuation of DEA in diaphragm like design.\textsuperscript{48}

Recently we developed a highly improved electromechanical DEA by grafting Azobenzene chromophores (azo for short) to a silicone rubber (SR).\textsuperscript{9} The enhancement of the actuation benefits from the high polarity of azo dyes and its good compatibility with SR matrix. However, the dielectric constant of SR matrix is too low and the fabrication process of chemical crosslinking is complicated, which should deteriorate the merit of this system.

Herein we developed a simpler dielectric elastomer by blending the azo dye with a thermoplastic polyurethane (TPU). TPU have a high intrinsic dielectric constant ($\varepsilon\sim8.0$ at 1 kHz) compare to other DEA such as acrylate (3M VHB) ($\varepsilon\sim4.7$ at 1 kHz) and silicone ($\varepsilon\sim3.0$ at 1 kHz). And due to the strong intermolecular interactions between azo and TPU, elastomer with high permittivity, good elasticity, and enhanced electromechanical actuation are achieved under low loading of azo dyes. The dielectric permittivity, mechanical properties and electromechanical actuation of diaphragm-type actuators of resultant Azo/PU blends are reported and discussed in details.
2 Experimental

2.1 Materials

A polyether-based polyurethane (Elastollan 1185A®) was purchased from BASF and used as received. N,N-Dimethylformamide (DMF) was purified using CaH$_2$ and stored over A4 molecular sieves. The 4-diethanolamine-4’-nitro-azobenzene, also found under the denomination of disperse red 19 (DR19), was synthesized as reported in a previous work.$^9$

2.2 Preparation of dielectric elastomer films

Thin film of DR19 and PU blends (denoted as Azo/PU) were prepared by a solution casting method. PU granules were firstly dissolves in DMF under a concentration of 10wt%. The mixture was magnetically stirred at 50°C until a visually homogeneous solution was obtained. After a certain amount of DR19 solution in DMF (10wt%) was added, the mixture was homogenized by stirring for another 2h. Then, the mixture was casted onto a pre-cleaned glass plate with a doctor blade film applicator, dried under vacuum at 80°C for 24h. After cooling down to room temperature, the film was carefully peeled off from the glass plate and placed in vacuum oven at 130°C for at least 24h to eliminate any residual solvent. The Azo/PU blend films containing DR19 of 1phr (per hundred resins), 2phr, 4phr and 8phr were prepared, which are denoted as Azo1, Azo2, Azo4 and Azo8, respectively. Thin film of pure PU was also prepared for control under the same procedures and is denoted as Neat PU. The thicknesses of the obtained films were controlled to be around 30µm.

2.3 Characterization
Infrared spectra of samples were measured by using a Nicolet 5600 IR spectrometer in the 400-4000cm\(^{-1}\) wavenumber range. Computational treatment was done on all spectra to smooth obtained curves.

Dielectric properties of the films were measured by using an impedance analyzer (Agilent 4294A) over the frequency from 1kHz to 10MHz. Silver electrodes had been coated prior to measurement on specimens with a 1cm\(\times\)cm square shape. Mechanical measurements were carried out by using a Shimadzu AG-IC universal tester under a constant 50mm/min strain rate at room temperature. Samples were prepared by cutting the thin films into a 30\(\times\)10 mm\(^2\) rectangular shape before testing. Samples with a 50\(\times\)10 mm\(^2\) rectangular shape were used for the loading-unloading test. Samples were loaded till 100% and maintained for 5s before the unloading began. The unloading was stopped at a force equal to 0 kN and maintained for 5 s. The Young’s modulus was obtained by linearization of each stress-strain curve at small strain inside the elastic domain (strain<10%).

The actuation performance of dielectric elastomer films was tested using a 16 mm diameter diaphragm type actuator. Elastomer films were coated with graphite powder on each surface as electrodes. The voltage was provided by a high voltage supplier Boher HV equipped with a Tektronix P6015A high voltage amplifier and linked to a DPO2012B Digital Phosphor Oscilloscope. The actuated displacements of elastomers films were monitored by using a 635 nm laser sensor (Panasonic HL-G105), which focused on the center of the actuator and connected to a personal computer.

In all characterization, experiments were carried out at least three times at room temperature under the same conditions for repeatability.

3 Results and discussion
3.1 Dielectric properties

Frequency dependences of dielectric permittivity and loss of neat PU and Azo/PU blends are shown in Fig 1. Compared to neat PU, the permittivity of Azo/PU blends shows a large increase under a small content of DR19 meanwhile the dielectric loss remains relatively low (below 0.17). The permittivity at 1 kHz increases from 8.0 for the neat PU to 11.1 for the Azo1 and even reaches 35.6 for the Azo4, which withstands a 38.6% increase for the former and more than a 4-fold improvement for the latter. Surprisingly, the Azo4 displays the biggest value of dielectric constant, which is even higher than that of Azo8.

![Figure 1: Frequency dependence of dielectric permittivity (a) and loss tangent (b) of Azo/PU blends with different DR19 content](image)

A good dispersion of strong polar DR19 within the TPU matrix could explain the improved dielectric constant obtained for the Azo/PU blends. The dielectric loss curves of Azo/PU blends for various DR19 content represented in Fig 1(b) could correlate this
assumption. Another possible reason is a good alignment between the PU dipoles and the DR19 dipoles. Fig 1(b) shows the variation of the loss tangent of Azo/PU blends over the frequency for various DR19 content. The incorporation of the DR19 modifies the shape of this curve and the frequency of its maxima. The dielectric loss at high frequency represents the rotation of intrinsic PU dipoles. The variation of the maximal dielectric loss frequency is in correlation with the dielectric permittivity of the Azo/PU blends. This indicates that the DR19 may help the dipole rotate faster due to their high dipole moment (9 Debye). This result also suggests an effective blending of the DR19.

Under higher filling concentration of DR19, a local maximum at lower frequency appears. At the same time a decreasing of the dielectric permittivity starts. This could represent a steric hindrance from the matrix or another DR19 which are correlated with the dispersion of the dyes. A different structure of the blend at higher concentration of DR19 is thus expected. However, similar azo-compound has been found to easily form aggregates\(^\text{[49,50]}\) that may also explain a high value of dielectric constant and explain the apparition of the loss at lower frequency.\(^\text{[51]}\) DR19 aggregates are formed by dipole-dipole, and π-π interactions. A single DR19 molecule and the supposed aggregate are represented in Scheme 1.

![Scheme 1: Single DR19 (a) and DR19 aggregate representation (b)](image-url)
To obtain information about the dipole orientation ability, the dielectric relaxation time was studied by using Nyquist plots of the complex impedance, which is shown in Fig 2. The real part of the impedance $Z'$ corresponds to resistance while the imaginary part $Z''$ corresponds to capacitance of a dielectric material. The introduction of DR19 into the PU matrix results in an increase of both the real and imaginary part of the impedance. Fig 2(a) shows that the curves of neat PU and Azo/PU blends are parabolas. The asymmetry of the neat PU and Azo1 curves reflects a heterostructure. This is due to microphase separation of hard and soft domains within the PU matrix. Adding DR19 fillers can further increase the heterogeneity of the structure.

Figure 2: Nyquist plots (a) and equivalent electrical circuit (b) of Azo/PU blends with different DR19 content

At higher DR19 content, $Z''$ could be decomposed onto two parabolas. In a Nyquist plot, each parabola (or semi-circle) reflects an occurrence of dipolar relaxation process. By identification, the parabola at high frequency (low $Z'$ value) represents the TPU dipoles relaxation. Whereas the parabola at low frequency represents the DR19 dipoles relaxation inside the matrix dipoles.\(^{[50]}\) The change of shape between Azo1 and Azo2 may indicate the
formation of aggregates. The dielectric relaxation time of each blend was determined using
the frequency on which the top of the parabolic curves appears. The observed relaxation times
($\tau_{\text{obs}}$) were summarized in Table 1 as a function of the DR19 content.

Table 1: DR19 dependence of the dielectric relaxation time

<table>
<thead>
<tr>
<th>DR19 content (wt%)</th>
<th>$\tau_{\text{Dloss}}$ (µs)</th>
<th>$\tau_{\text{obs}}$ (µs)</th>
<th>$\tau_{\text{calc}}$ (µs)</th>
<th>$\tau_{\text{geo}}$ (µs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.22 /</td>
<td>0.41 /</td>
<td>0.63 /</td>
<td>2.3 /</td>
</tr>
<tr>
<td>1</td>
<td>0.10 /</td>
<td>0.26 /</td>
<td>0.26 /</td>
<td>0.71 /</td>
</tr>
<tr>
<td>2</td>
<td>0.14 5.0</td>
<td>0.40 5.8</td>
<td>0.32 15.8</td>
<td>4.1 14.2</td>
</tr>
<tr>
<td>4</td>
<td>0.10 4.4</td>
<td>0.15 7.94</td>
<td>0.12 17.7</td>
<td>0.82 2.25</td>
</tr>
<tr>
<td>8</td>
<td>0.14 1.6</td>
<td>0.37 4.44</td>
<td>0.44 8.85</td>
<td>7.0 12.5</td>
</tr>
</tbody>
</table>

The observed relaxation times are linked to the Nyquist plot by reading the Fig 2(a) form left to right. Calculated results of relaxation times from Gaussian deconvolution ($\tau_{\text{calc}}$) and from dielectric loss ($\tau_{\text{Dloss}}$) are listed in Table 1 for comparison. Relaxation times display the same variation under these three methods. Due to difficulty to see clearly the second relaxation time in Fig 1(b), it has been chosen to compare the observed and calculated result from Fig 2(a). The value of the second relaxation is very different in the calculated result but in better correlation with the dielectric loss represented in Fig 1(b). The presence of aggregates is thus highly expected even if a better knowledge of structure should be obtained.

Nyquist plot are widely used to find equivalent electrical circuit of materials.\cite{51} Each semicircular arc in the impedance pattern as shown in Fig 2 can be attributed to a resistance (R) and capacitance (C) associated in parallel. A RC parallel circuit is also used to represent a parallel plate capacitor. Constant phase element (CPE) is a physical element often use in equivalent electrical circuit to take non ideality in consideration.\cite{52} A resultant equivalent
circuit of the Azo/PU blends is represented in Fig 2(b). The addition of DR19 changes the value of R, C, and CPE of the equivalent circuit.

To obtain approximate value of R element, geometrical analyses have been realized as elsewhere.\cite{51} Because our materials showed parabolic in place of semi-circle curves, the width (FWHM) has been taken in place of the diameter of semi-circle to determine R. This value is listed as \( R_{\text{geo}} \) in Table 2. The relaxation time calculated with this geometrical analysis is referred as \( \tau_{\text{geo}} \) in Table 1. The capacitance C could be obtained using the relation:

\[
\tau_{\text{geo}} = 1/f = R_{\text{geo}}C_{\text{geo}} \quad (3)
\]

where \( \tau \) is the relaxation time, \( C_{\text{co}} \) is the value of C at the peak of \( Z'' \) and is recorded in Table 2 for various DR19 content in Azo/PU blends. As expected, values issued from geometrical study have a variation identical to the evolution of the Z pattern in the Fig 2(a). Diffusion process at low frequency could be taken into consideration by insert a diffusion Warburg Element (W). It is represented in Z pattern by a straight line. The beginning of such line could be seen for the Azo1 near 8kHz, close to the lower value of our frequency range used. In addition the parabolas don’t pass through the origin of the Nyquist plot; thus a resistance (Rs) has been added in series.

<table>
<thead>
<tr>
<th>Name of sample</th>
<th>( R_{\text{geo}} ) (k( \Omega ))</th>
<th>( C_{\text{geo}} ) (pF)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat PU</td>
<td>20.6</td>
<td>4.7</td>
</tr>
<tr>
<td>Azo1</td>
<td>22.4</td>
<td>32.2</td>
</tr>
<tr>
<td>Azo2</td>
<td>11</td>
<td>1.7</td>
</tr>
<tr>
<td>Azo4</td>
<td>26.2</td>
<td>48.3</td>
</tr>
<tr>
<td>Azo8</td>
<td>6.6</td>
<td>13.8</td>
</tr>
</tbody>
</table>
Data listed in Table 2 give some primary observation about expected actuation performance for Azo/PU blends with different concentration of DR19 filled. However without the CPE, only approximation could be done. Azo2 has a large value of resistance and an equal capacitance compare to the neat PU. This blend could have lower actuation performance than the neat PU. Meanwhile Azo1 with a similar resistance to the neat PU possesses a capacitance seven times higher. A great improvement of actuation is thus expected for this blend. The Azo8 has a resistance and capacitance values somewhat close to the neat PU, meanwhile Azo4 shows a very large increase of the value for these two components. It is therefore difficult to predict actuation results with only the dielectric analysis for the Azo4 and Azo8.

3.2 Mechanical Properties

All materials are stretchable and could withstand large strain. The stress response of Azo/PU blends are represented in Fig 3. All samples didn’t break but unclamp at various strain. This may be due to the thickness of the films tested. Therefore, the elongation at break will not be studied here. However some observations could be pointed out. It seems that at a given strain, the stress is higher while increasing the DR19 content. This behaviour is similar to other filler reinforced polymers.\textsuperscript{[53-55]} Fig 3(b) shows the blends response at low strain (<50%). Only at this strain, it seems that Azo2 need lower stress to reach the same strain value than Azo1. It appears that the Young’s modulus increases while the DR19 content is increasing. From Fig 3, another observation is made. With the increasing concentration of DR19, there is a slight displacement of the yield point moving to lower strain. This may correspond to a change of plasticity inside the TPU matrix.
The stress softening of Azo/PU blends were performed using loading-unloading curves at 100% deformation as represented in Fig 4. Some curves seems not stop at a stress value of 0, however the difference is under 1MPa that is below to 0.01N sensitivity of the force sensor. The residual strain over loading-unloading cycles is represented in Fig 4(f). It seems that adding the DR19 into the TPU matrix make decrease the residual strain. This behaviour is surprising regarding the literature.[54, 56] However, the increase in residual strain is less important when the number of loading-unloading cycles increased for all Azo/PU blends and an expected Mullins effect begins to appear after 5 cycles. These observations are in agreement with the literature.[54]

The TPU is supposed have disruption of Hydrogen bond and disentanglement of chain that reform in another configuration during a loading-unloading cycles.[57] Moreover, the 5s maintained time may let enough time for this blend to rearrange its macromolecular structure closer to its initial state.[56] The authors think that the presence of DR19 changed the structure of the PU. The TPU molecular chain could not deform as freely as in the neat PU. Therefore,
the macromolecular structure was less modified. DR19 may create microstructures, thus enhanced heterogeneity in structure as seen in Fig 2. These microstructures, delimited by the rigid DR19, reduced the deformation of the TPU chain and increased the stress when the strain is increasing as shown in Fig 3. Therefore, we supposed that Azo4 have more microstructures, due to a better dispersion of DR19, than the Azo8. This good dispersion was a proposed reason for the high dielectric permittivity observed with Azo4 in Fig 1. In addition it can be seen in Fig 4(f) that the residual stain in Azo8 is nearly constant. We could thus assume in regards of the previous results that the blend with 8phr DR19 content possesses aggregates. The high difference in residual strain between the first cycles of Azo/PU blends is supposed coming from slipping of DR19.\textsuperscript{[57]}

Table 3 lists the Young’s modulus, dielectric constant and the actuation sensitivity $\beta$ of Azo/PU blends. Only Azo8 shows a lower $\beta$ than that of the neat PU due to the too high Young’s modulus. This result suggests that, except the Azo8, all the blends should theoretically exhibit better actuation performance than the neat PU.

Table 3: Young’s modulus, dielectric constant and $\beta$ with various content of DR19

<table>
<thead>
<tr>
<th>Name of the material</th>
<th>Young’s modulus $Y$ (MPa)</th>
<th>Dielectric constant $\varepsilon$ at 1 kHz</th>
<th>$\beta = \varepsilon/Y$ (MPa$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat PU</td>
<td>22</td>
<td>8.0</td>
<td>0.365</td>
</tr>
<tr>
<td>Azo1</td>
<td>24.1</td>
<td>11.1</td>
<td>0.463</td>
</tr>
<tr>
<td>Azo2</td>
<td>25.3</td>
<td>11.3</td>
<td>0.444</td>
</tr>
<tr>
<td>Azo4</td>
<td>30.3</td>
<td>35.6</td>
<td>1.18</td>
</tr>
<tr>
<td>Azo8</td>
<td>51.8</td>
<td>13.8</td>
<td>0.266</td>
</tr>
</tbody>
</table>
Figure 4: Loading-unloading curves of Azo/PU blends with 0phr (a), 1phr (b), 2phr (c), 4phr (d) and 8phr (e) of DR19 content and the accumulation of residual strain over loading-unloading cycles (f)
### 3.3 Actuation

A diaphragm design, as shown in Scheme 2, was chosen for the actuation performance assessment.\cite{59} Similar to widely reported diaphragm actuators in literature, the depletion strain (S), which is obtained by dividing the displacement (h) in vertical direction to the initial thickness of the dielectric film was employed to represent the electromechanical actuation.

**Scheme 2: Diaphragm-type actuator design**

Fig 5(a) shows the actuation response for different Azo/PU blend films as a function of the electric field until the electrical breakdown occurred. The electric field is obtained by dividing the applied voltage to the initial thickness of the DEA.\cite{30} In the case of the Azo4, the electric arc during breakdown (25kV/mm) is very strong. To protect our material it has been chosen to stop the experiments at 20kV/mm before the breakdown occurred. Curves shown in Fig 5 are fitted curves of experimental data. Despite a low electromechanical actuation of the Azo2, other blends showed better actuation performance than the neat PU.
Electromechanical response of the blends shown in Fig 5(a) could be decomposed into 3 stages. During the first stage, no actuation could be seen as previously reported in literature for other DEA. Then, at a various electric field depending the blend, the thin film DEA begin to have out-of-plane actuation (depletion strain) further follow by a saturation as seen for the Azo1 around 45kV/mm. This behavior is consistent with the literature for conventional DEA and PU. We remark a second increase (52kV/mm) in depletion strain for the Azo1. However this could be an artifact coming from the approaching electrical breakdown. Error bar calculated from standard deviation to the mean are represented in Fig 5(a). All results are included inside a 10% margin. Therefore the error is increasing parallel to the depletion strain.
Conventional piezoelectric MEMS are usually used at low electric field (<20kV/mm) that may not hurt human. Electromechanical response of our materials at such electric field is shown in Fig 5(b). At low electric field, all the blends perform equally or better than the neat PU, confirming that the introduction of the DR19 is efficient to improve the actuation performance of the TPU. The maximum depletion strain of Azo/PU blend containing 1phr of DR19 is 2250%, which is about 26 times higher than that of the neat PU. At low electric field the difference is even higher. Galineau et al.\cite{61} have reported great improvement in low electric field actuation with Carbon Black filled PU, but the present result is even higher. Surprisingly, in both studies the blend containing around 1wt% of filler display the best actuation.

In addition, Azo1 and Azo2 show higher breakdown strengths that the neat PU. The breakdown strength of Azo/PU blends are represented in Fig 5(c). The error bars was calculated as in Fig 5(a). Contrary to the depletion strain, the breakdown strength has a large margin error of around 20%. This represents 5 to 12 kV/mm difference from the lowest (Azo8) to the highest (Azo2) breakdown strength recorded. The decreased breakdown strength of Azo4 and Azo8 should come from aggregates as discussed above. The electrical breakdown strength of polymeric dielectric material is highly correlated to the free volume and the energy cohesive density between different macromolecular chains. The later is expected for the Azo1 and Azo2 blends to explain their high breakdown strength.

The squared electric field dependence of Azo/PU blends actuation is represented in Fig 5(d) for low electric field values. Curves are fitted with linear lines. It result a good approximation between the fitting lines and the curves as showed in literature.\cite{9, 60} That linearization is no more true for the Azo4 at 330(kV/mm)^2 (18kV/mm, see Fig 5(b)) when the steady increase appeared. This linear dependence to the squared electric field is in correlation with the equation 1 presented in the introduction.
However several new observations could be done. The Azo1 have the highest director coefficient but do not have the highest dielectric permittivity or dielectric sensitivity defined by equation 2. Azo4 and Azo8 have similar value of director coefficient despite very different dielectric results. Corrected the equation 2 with the square electrical breakdown as in literature$^{[27]}$ do not change this behavior. But we should highlight that the Azo4 compound has its steady increase in actuation sooner than the other blends.

Moreover, Figs 5(a) and 5(b) show that the actuation performance is driven by a complex mechanism. Usual figure of merit could not predict accurately the electromechanical response of our system. Results from impedance analysis in section 3.1 are in contradiction with the supposed actuation performance deduced from the dielectric sensitivity $\beta$ in section 3.2 for Azo2 and Azo8. Observations of Fig 5 indicate that the impedemmetry, a powerful dielectric structural analysis, is in better adequation with the experimental result than $\beta$. A similar result was obtained in literature with PVC gels$^{[63]}$, but in our knowledge, it is reported for the first time with PU here. This led us to affirm that it is the structure that drives the actuation performance of the blends with the PU matrix. The importance of microstructure for actuation property has been reported recently.$^{[48]}$ Thus structural analysis of our blends is following.

3.4 Structure characterization

Infrared spectroscopy as a sensitive analysis method of bonding was used to study the structure variation of the Azo/PU blends. An unmodified peak near 500cm$^{-1}$ was used to normalize spectra of Azo/PU blends that are reported in Fig 6. As explained above, the DR19 are linked to the intrinsic dipole of PU most located in the hard domain. Three different ways are available for the DR19 to form hydrogen bonds with the PU matrix. From the nitro function group with the N-H, the two hydroxyl functions with both the N-H and the carbonyl
and a π-π interaction with the benzene rings originate from the MDI. Analysis of C=O, NH bands are thus further examined in details.

![Normalized FTIR spectrum of Azo/PU blends](image)

**Figure 6:** Normalized FTIR spectrum of Azo/PU blends

It is well known that in PU the stretching vibration of C=O appears under the form of two peaks, one near 1730cm⁻¹ representing free C=O and the second near 1705cm⁻¹ for hydrogen-bonded C=O. FTIR spectra of blends between 1650-1800cm⁻¹ are recorded in Fig 7 with the ratio of the area of the hydrogen-bonded C=O at 1704cm⁻¹ to the area of the free carbonyl band at 1731cm⁻¹. Areas were calculated using two Gaussian fitting curves. It appears in Fig 7 that all blends display a lower ratio than the neat PU. There is slightly less hydrogen-bonded and more free carbonyl groups in the TPU to be linked with the DR19. The difference is more pronounce for the Azo1, confirming that it has a special structure compared to other blends as suggested in Scheme 3.
Figure 7: DR19 content dependence of the two carbonyl bands with their Gaussian fitting curves and the corresponding area ratio.

Scheme 3: Supposed structure of Azo1 blend

The N-H stretching vibration at 3330 cm\(^{-1}\) is shown on Fig 8 as function of the DR19 content. For the Azo1, the peak shifts to higher wavenumber, suggesting a decrease in the...
strength of the hydrogen-bonded N-H group of pure PU. Correlated with Fig 7 this shows an N-H/C=O disruption bond of the PU by incorporating the DR19. In the case of the Azo1, it appears that the dye linked with the NH group of the urethane through the nitro function leading on a weaker hydrogen-bonded strength. This bond between the DR19 and the matrix also align the dipolar moment of the dye with that of the PU explaining the high dielectric permittivity obtained and a similar dielectric loss to the neat PU.

Figure 8: N-H stretching band variation with various DR19 content

 Whereas the other blends seems to bond with the carbonyl or NH function of PU matrix using the hydroxyl function or the π-π interaction between two layers included in a hard domain of the TPU. The rigidity of the DR19 molecule and the relative softness of the PU (with limited hard domain) limit the number of hydrogen bonds between them and the structural organization is explaining the light modification on the hydrogen-bonded carbonyl bands. The higher ratio of free carbonyl group in the Azo4 compare to the Azo2 and Azo8 could be explained by the formation of bigger aggregates that freeing the carbonyl function of the PU or by single DR19 molecule as in Azo1.

In order to understand if the DR19 is hydrogen-bonded to the PU at the interface between hard and soft domain or only inside a hard domain, the symmetrical and
asymmetrical stretching of CH₂ characteristic of the soft segment is investigated. These peaks were fitted using Gaussian curves and the corresponding areas are listed in Table 4. It appears that the Azo1 displays more asymmetrical stretching than the other materials. We could thus assume that in this blend, the DR19 is bonded with the soft and the hard domain. This correlates the previous assumption made above about the orientation of the dye compare to the PU dipoles, which reduces the probability of the DR19 to be inside the hard domain.

The results of the other blends are quite similar to the neat PU. The lower CH₂ symmetrical stretching of the Azo4 and Azo8 may be due to higher dispersion of aggregates in the soft segment of the matrix. It could be deduced by the evolution the CH₂ stretching bands that DR19 prefer to make H-bond with the hard domain than be dispersed into the soft domain. This result also confirms the three available ways for DR19 to hydrogen bond with the TPU as cited previously. The reduced free volume and higher number of aggregates explain the low dielectric breakdown strength in Azo4 and Azo8.

Table 4: DR19 content dependence of the area variation of the C-H bending fitted curves

<table>
<thead>
<tr>
<th>DR19 content (%w)</th>
<th>Peak 1 Area A1 (2950cm⁻¹)</th>
<th>Peak 2 Area A2 (2913cm⁻¹)</th>
<th>Peak 3 Area A3 (2850cm⁻¹)</th>
<th>A1/A2</th>
<th>A1/A3</th>
<th>(A1+A2)/A3</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>13.92</td>
<td>7.81</td>
<td>19.72</td>
<td>1.78</td>
<td>0.71</td>
<td>1.10</td>
</tr>
<tr>
<td>1</td>
<td>1.82</td>
<td>14.60</td>
<td>4.87</td>
<td>0.12</td>
<td>0.37</td>
<td>3.37</td>
</tr>
<tr>
<td>2</td>
<td>13.61</td>
<td>6.09</td>
<td>17.90</td>
<td>2.23</td>
<td>0.76</td>
<td>1.10</td>
</tr>
<tr>
<td>4</td>
<td>13.87</td>
<td>7.05</td>
<td>18.57</td>
<td>1.97</td>
<td>0.75</td>
<td>1.13</td>
</tr>
<tr>
<td>8</td>
<td>16.87</td>
<td>6.47</td>
<td>20.69</td>
<td>2.61</td>
<td>0.82</td>
<td>1.13</td>
</tr>
</tbody>
</table>
Using the supposed structure of aggregates (Scheme 1), we can suppose that aggregates are generally formed by two DR19 molecules. It results that aggregates are likely to form two hydrogen bonds with both the NH and C=O function of the TPU matrix. This explains why only Azo8 blend has lower wave-number of NH band. We can also conclude that the presence of “single stage” DR19 molecule bonded with the hard domain and dispersed in soft domain in addition of aggregate explain the results for Azo4. A proposed structure for Azo/PU blends for each DR19 loading is represented in Scheme 4.

Scheme 4: Proposed structure for Azo/PU blends with (a) 1wt%, (b) 2wt%, (c) 4wt% and (d) 8wt% of DR19

4 Conclusion

A strong polar azobenzene, DR19, was successfully blended with a polyether-based polyurethane. The azobenzene loading affects the mechanical, dielectric and electromechanical actuation performances of the polyurethane. The blend containing 1wt% of DR19 showed the highest actuation (nearly 2300% depletion strain). In addition, the breakdown strength was increase by 86%. Whereas the Azo/PU blend containing 4wt% DR19 had a better electromechanical sensitivity β.
FTIR spectra showed that the linkage between the azo dye and the polymer matrix is due to the hydrogen bonds through the N-H and/or C=O functions from the carbamate in the hard segment. The FTIR analysis proved that the specific structure of the 1wt% and 4wt% azobenzene blends explain their exceptionally high electromechanical performances and high dielectric constant. A structure of Azo/PU blends with different azo dye content was proposed.

The present results are encouraging for further use in tactile displays, wearable electronic devices and human-machine interfaces. However several tests are ongoing to better understand the structure-properties relation for all the blends. The knowledge of the influence of prestraining on our blends, that was proven to improve actuation of acrylates and silicon actuators, is under investigation.

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