Slot-die coating of an on-the-shelf polymer with increased dielectric permittivity for stack actuators

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ABSTRACT

Nitrile–butadiene rubbers (NBR) have been extensively used as dielectric materials due to their commercial availability, excellent mechanical properties, glass transition temperature below 0 °C, and increased dielectric permittivity owing to the presence of polar nitrile groups. Despite these advantages, their processability is poor and cross-linking into thin films is a challenge. Cross-linking requires long times, temperatures exceeding 160 °C, and an inert atmosphere. Such cross-linking conditions are incompatible with the continuous manufacturing process of stack actuators.
Here we developed a NBR that can be easily processed into thin films, cross-linked fast and on-demand by UV-induced thiol-ene reaction in the presence of dimethoxy-2-phenylacetophenone initiator and 2,2’-(ethylenedioxy)diethanethiol cross-linker. The mechanical properties of the NBR can be easily tuned by the amount of cross-linker used. Additionally, a semi-automated manufacturing process for stack actuators is presented. Here we slot-die coat the dielectric and spray-coat the electrode through a mask. Because of the commercial availability of the starting materials, an easy and robust protocol for cross-linking, and reproducible manufacturing, it can be envisioned that this material has the potential to replace the well-known acrylate film, VHB™, which engineers often use to construct dielectric elastomer actuators in different prototype devices.

KEYWORDS: Dielectric elastomer actuators, high dielectric permittivity elastomer, stack actuators, thiol-ene cross-linking, nitrile-butadiene rubber

INTRODUCTION

The synthesis of artificial muscles with properties reminiscent of natural muscle continues to be a great challenge for chemists and materials scientists.1 Natural muscles possess a unique combination of properties such as high strength, extensibility, and resilience. Similar to natural muscles, elastomers can reversibly change their shape under mechanical stress.2 When properly designed, shape changes in elastomers can be induced by different stimuli such as temperature, pH, humidity, light, magnetic or electric field.3,4 Elastomers that respond to an electric field are highly attractive due to their relatively simple operation and fast response time.

Dielectric elastomer actuators are stretchable capacitive devices in which the dielectric is a thin elastomer insulator film sandwiched between two electrodes made from thin elastomer
conductors. When the capacitor is charged, an electrostatic force is generated. This force stretches the elastic capacitor, making it thinner and larger in area. Thus, the capacitor converts electrical energy directly into mechanical work. After the voltage is turned off, it relaxes back to the original shape. In addition to lightweight and noiseless operation, actuation is possible at different frequencies and temperatures. Arguably, the greatest advantage of this technology is the possibility of controlling the actuation by the voltage. Because of the simple construction and operation, this technology gained significant attention from academia and industry. Applications include pumps, valves, tactile displays, adaptable lenses, soft robots, muscle replacement, medical devices, sensors, and generators. Despite the immense application range of this technology, the synthesis of novel polymers with improved properties has been given way too little attention. Most devices are constructed from a commercial polyacrylate foil, the VHB. This material was designed to function as glue and thus only partially meets the properties needed for a dielectric film suited for actuators. However, its commercial availability allowed prototype manufacturing. The whole development has now reached a phase in which the practical implementation of the technology critically depends upon whether better materials can be provided. Elastomers are needed, which not only have an increased dielectric permittivity but can also be efficiently processed into stack devices consisting of many single actuators stacked on top of each other and connected in series.

We have recently shown that the chemical modification of polysiloxanes with polar groups can afford elastomers with high dielectric permittivity ($\varepsilon' = 18$), a dielectric breakdown field that can reach 100 V$\mu$m$^{-1}$, and remarkable electromechanical properties. Despite the great performance of these materials in single membrane actuators, there is a limitation in using them for manufacturing stack actuators. Namely, the access to rather expensive manufacturing
equipment and cleanroom facilities due to possible contaminations caused by uncross-linked silicones is hindered. Although solutions for this issue are actively pursued, we also turn our attention to commercial products, which have similar properties as our polar silicone when uncross-linked, but do not pose problems concerning eventual contamination. This will allow us to evaluate the feasibility of certain equipment for manufacturing multilayer actuators before expensive investments are being done, including to devote a cleanroom solely to polysiloxanes. Once the whole process is fully understood, all promising materials will be ‘fed’ into it.

Nitrile – butadiene rubbers (NBR) with different content of nitrile groups are commercially available and were intensively explored due to their elastic and dielectric properties for applications such as electronic and ionic actuators. The nitrile group content and the cross-linking density strongly influence the dielectric properties. For instance, the dielectric permittivity increased from 7.6 to 9.6 and reached a value of 10 with increasing nitrile content from 23% to 35% to 40%, respectively. Additionally, to improve the dielectric permittivity and electromechanical sensitivity of NBR, different fillers such as BaTiO₃, TiO₂, and conductive fillers were used. The potential of NBR was intensively explored not only in single membrane actuators, but also in stack actuators. A common characteristic of all NBR used in actuators is the peroxide cross-linking reaction. This, however, has the severe disadvantage that it is sensitive to oxygen, which renders it impossible to work in a normal atmosphere. Furthermore, temperatures exceed 160 °C and reaction times are long. Therefore, peroxide curing is not suitable for the continuous manufacturing of stack actuators.

Here, we describe a NBR that can be cross-linked on-demand in air and allows easy manufacturing into thin films by slot-die coating. The formed films have increased dielectric permittivity and mechanical properties that can be tuned by the amount of cross-linker used.
Additionally, this material allowed us to develop a process to stack actuators by slot-die coating the dielectric and spray-coating the electrode through a mask. The developed process is reliable, easy to scale up, and easy to adapt to other promising materials, such as our polysiloxanes.

**MATERIALS AND METHODS**

Poly(acrylonitrile-co-butadiene), dicarboxy terminated (PANB) \( (M_n \sim 3,800, \text{ acrylonitrile 8-12 wt. \%}) \), 2,2′-(ethylenedioxy)diethanethiol (CL), and dimethoxy-2-phenylacetophenone (DMPA) were purchased from Sigma Aldrich and used without purification. The characterization of the starting polymer can be found in the supporting information (Figures S1, S2). The electrode is a blend of graphite/carbon-black blend Elcocarb B/SP from Solaronix. Before use, the electrode was diluted with ethanol at a 1:2 ratio (electrode:ethanol).

UV irradiation was done with a UV lamp from Peschl Ultraviolete SwiftCure HL-250 \((\approx 35 \text{ mW/cm}^2)\). For irradiation, the lamp was placed at 20 cm distance to the polymer films.

Perkin Elmer Pyris Diamond DSC instrument was used for DSC investigation. Two heating steps and one cooling step were performed with the rate of 20 °C/min in the temperature range of −90 to 50 °C under a nitrogen flow \((50 \text{ mL min}^{-1})\) in aluminum crucibles shut with pierced lids and using about 10 mg sample mass. The second heating step was used to determine the \(T_g\).

Thermogravimetric analysis (TGA) was conducted on a Netzsch TG 209 F1 in an inert atmosphere. The uniaxial stress-strain and cyclic stress-strain tests were conducted on a Zwick Z010 tensile test machine. We performed the tests on specimens with a gauge of 2 mm in width and 18 mm in length. The specimens were strained with a speed of 50 mm/min. The curves were averaged from at least three different samples per material. The elastic modulus \((Y_{10\%})\) was calculated from the slope of the curves by applying a linear fit to the points within 10% strain.
The dielectric breakdown field was evaluated using a previously described setup. The dielectric breakdown field \( E_b \) of a series of dielectric elastomers, An, was measured by placing the films between two flat electrodes with a 1 mm\(^2\) area embedded in an epoxy resin. The voltage was gradually increased until the breakdown occurred. Weibull probability plots were performed using Origin, version 2020 (OriginLab Corporation, Northampton, MA, USA). Permittivity measurements were performed in the frequency range from \( 10^{-1} \) Hz to \( 10^6 \) Hz using a Novocontrol Alpha-A frequency analyzer. The VRMS (root mean square voltage) of the probing AC electric signal applied to the samples was 1 V. The thickness of the film was measured by a micrometer gauge with an uncertainty of \( \pm 5 \mu m \). Two stainless steel discs with a diameter of 20 mm served as electrodes, which were either placed on the films or were separated by three glass fibers with a diameter of 100 \( \mu m \) \( \pm 5 \mu m \) for the liquid samples. Before measurement, the samples were carefully dried in a vacuum oven at 60 °C.

Electromechanical tests on single layers were performed using circular membrane actuators at ambient temperature and humidity. The films were biaxial prestrained by 7% and fixed between two circular frames with an inner diameter of 2.5 cm. Circular electrodes (8 mm diameter) of carbon black powder were applied to each side of the film. A FUG HCL- 35-12'500 high voltage source served as a power supply for actuator tests. The voltage was increased by 100 V steps every 2 s up to a maximum of 5.6 kV. The actuation strain was measured optically as the extension of the diameter of the electrode area via a digital camera, using an edge detection tool of a LabView program to detect the boundary between the black electrode area and the transparent silicone film. The maximum resolution of LabView was 30 measurements per second. The stack actuators were tested by increasing the voltage within 25 s from 0 V to a predefined voltage and then decreased to 0 again within 25 s, while a Baumer X023 laser measured the change in the stack thickness.
A UVHAND 250 GS H1 mercury vapor UV lamp from Dr. Hoenle AG was used for cross-linking the films.

**Preparation of thin Films**

A homogenous mixture of PANB, CL, and DMPA was processed into thin films by the Doctor Blade coating technique and cross-linked by irradiating with UV light for 5 min. The amount of CL used was tuned. The formed dielectric elastomers are named An (see Table 1).

**Table 1.** Reagents and amounts used for the synthesis of materials An.

<table>
<thead>
<tr>
<th>Sample</th>
<th>PANB [g]</th>
<th>CL [µL]</th>
<th>DMPA [mg]</th>
</tr>
</thead>
<tbody>
<tr>
<td>A0</td>
<td>1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>A1</td>
<td>1</td>
<td>20</td>
<td>6</td>
</tr>
<tr>
<td>A2</td>
<td>1</td>
<td>30</td>
<td>6</td>
</tr>
<tr>
<td>A3</td>
<td>1</td>
<td>50</td>
<td>6</td>
</tr>
<tr>
<td>A4</td>
<td>1</td>
<td>100</td>
<td>6</td>
</tr>
<tr>
<td>A5</td>
<td>1</td>
<td>200</td>
<td>6</td>
</tr>
</tbody>
</table>

**Slot-die coating of optimized material A2**

PANB (1 g) was dissolved in ethyl acetate (0.2 mL) and mixed with CL (30 µL) and DMPA (6 mg). The ink was degassed before being loaded into a 20 mL syringe before connecting it to the slot-die coating machine. The coating was performed in a cleanroom using the following parameters: flow rate of 0.3 mL/min and speed of 0.005 m/min. The height of the slot-die was set using standard feeler gauges. The first dielectric layer was coated on a glass substrate and the obtained film was cross-linked by irradiating with UV light for 10 min. After cross-linking the dielectric film, the electrode was sprayed onto the dielectric using an airbrush system and a mask, completing a dielectric-electrode layer. Stack actuators consisting of five active layers were manufactured by repeating five times the above-mentioned steps. They were subsequently quality controlled by measuring their leakage current and those that passed the quality test were then stacked on top of each other, commencing in a final stack of 50 layers.
RESULTS AND DISCUSSION

Here, we introduce a promising dielectric elastomer that can be easily processed into high-quality thin films by either doctor blading or slot-die coating, and that can be cross-linked fast and on-demand under environmental conditions. The starting polymer is a commercial dicarboxy-terminated poly(acrylonitrile-co-butadiene) (PANB, $M_n \sim 3,800$ g/mol, acrylonitrile content 8-12 wt.%). This copolymer has a low $T_g$ due to the presence of flexible butadiene repeat units and has an increased polarity due to the presence of the polar nitrile groups. The low viscosity of the PANB polymer allows solvent-free processing into thin films. Its double bonds are used for cross-linking via a UV-induced thiol-ene click reaction.$^{50,51}$ Cross-linking is achieved by irradiating the thin films with UV light for 5 min (Scheme 1) using 2,2′-(ethylenedioxy)diethanethiol as cross-linker (CL). The amount of dithiol CL was varied to obtain materials with different stiffness and the cross-linking of the materials is proven by IR spectroscopy where new signals characteristic for the thioeter group appear (Figure S3). This resulted in a series of dielectric elastomers, $A_n$, with attractive mechanical and dielectric properties.

Scheme 1. UV-induced thiol-ene cross-linking reaction of poly(acrylonitrile-co-butadiene) (PANB) with DMPA initiators and 2,2′-(ethylenedioxy)diethanethiol cross-linker under normal atmosphere.

Figure 1 shows the thermal, mechanical, and dielectric properties of the synthesized materials. The thermal behavior of PANB and the cross-linked materials $A_n$ was investigated using differential
scanning calorimetry (DSC) in the temperature range between –100 °C to 50 °C (Figure 1a). The curves show only one glass transition, as is typical for random copolymers. The $T_g$ of all materials is significantly below room temperature, which is crucial for room temperature elasticity. With increasing CL amount, $T_g$ increases from –63 °C for uncross-linked PANB (A0) to –35 °C for A5.

The thermal stability was studied by thermogravimetric analysis (TGA) (Figure 1b) in an inert atmosphere between 30-700 °C. All samples showed excellent thermal stability up to 200 °C, with the main decomposition peak at about 460 °C.

**Figure 1.** Differential scanning calorimetry curves (a) and thermogravimetric analysis (b) of PANB (A0) and of cross-linked materials An; stress-strain curves of cross-linked materials An (The curves represent the average of three samples, whereby the strain at break is the strain of the sample that has the lowest strain, for the sake please see Table 2 and Figure S4) (c); cyclic tensile test of cross-linked materials A1-4 (d); and dielectric permittivity ($\varepsilon'$), dielectric loss ($\varepsilon''$), conductivity ($\sigma$), and dielectric loss ($\tan\delta$) as a function of the frequency of An (e).
The mechanical properties of the samples were investigated by tensile testing. Figure 1c shows the average stress-strain curves of three independent measurements. All stress-strain of all samples tested can be found in Figure S4. The increase in cross-linking density leads to a gradual decrease in the strain at break and an increase in stiffness. Elastic modulus and elongation calculated based on stress-strain curves are given in Table 2. Strain at break varies between 22% – 220%, while the elastic modulus ($Y_{10\%}$) ranges between 0.18 –7.84 MPa.

Uniaxial cyclic tensile tests were performed to study the elastic behavior of all materials, except for A5, which has a relatively low strain at break of only 33%. The cyclic stress-strain curves in Figures 1d show no hysteresis loop for A2-4 and a small hysteresis for A1, indicating excellent elastic properties. The good elastic properties of A2-4 are supported by the cyclic actuation tests, as will be shown later.

Broadband dielectric spectroscopy was used to investigate the dielectric properties of the obtained polymers at 20 °C and in a frequency range between 0.01–1 MHz. The dielectric permittivity ($\varepsilon'$), dielectric loss ($\varepsilon''$), conductivity ($\sigma$) and tan$\delta$ as function of frequency are shown in Figure 1e. The dielectric permittivity at low frequencies is higher than at high frequencies due to electrode polarization. Electrode polarization occurs at low frequencies because the ions move to electrodes and accumulate in thin layers forming a so-called space-charge region that causes an increase in the dielectric permittivity and a drop in the conductivity. At high frequencies, the field's time variation is shorter than the dipoles' relaxation time, and thus ions do not have sufficient time to accumulate at the electrodes. As a result, the dielectric permittivity decreases and the conductivity increase significantly at high frequencies. The values at 1 kHz were taken into account (Table 2) when comparing the An samples' dielectric properties with VHB. This frequency is considered high enough to avoid a contribution by the electrode polarization effect. The uncross-
linked PANB sample **A0** has a dielectric permittivity of around 6. By increasing the cross-linker amount and, thus, cross-linking density, the dielectric permittivity decreases gradually from 5.82 for **A1** to 3.43 for **A5**. This can be attributed to the decreased density of the polar nitrile group, increased cross-linker density, and reduced main-chain segmental motion due to a decrease of free volume reflected by the increased density (Table 2). A similar effect was observed before for acrylonitrile rubbers cross-linked by dicumyl peroxide.\(^\text{35}\) All prepared materials, except **A5**, have higher permittivity than VHB foil \((\varepsilon' = 4.5)\) and polydimethysiloxane elastomers \((\varepsilon' = 3.0)\). A slight change in the dielectric losses, and conductivity was also observed for cross-linked polymer, but at 1 kHz the values remain low for all analyzed samples \((\varepsilon'' < 0.07; \sigma < 4.5 \times 10^{-11} \text{ S cm}^{-1})\). The temperature-dependent dielectric properties of **A0** to **A5** (Figure S5-S10) were measured at temperatures ranging from –100 °C to 100 °C. These results show that the dipoles are fully mobile at room temperature.

Table 2 gives an overview of the density \(\rho\), glass transition temperature \(T_g\), elastic modulus \(Y_{10\%}\), elongation at break, dielectric permittivity \(\varepsilon'\), dielectric loss \(\varepsilon''\), conductivity \(\sigma\), and electrical breakdown field \(E_b\). The low elastic modulus, high dielectric permittivity, and high electrical breakdown field facilitate a higher actuation. For actuators, the dielectric elastomer should exhibit a \(T_g\) significantly lower than the operating temperature, high elongation at break, and conductivity in the region of electric insulator materials. Sample **A1** has the lowest \(T_g\), highest elongation at break, highest dielectric permittivity, and lowest elastic modulus, but is viscoelastic. Thus, **A2** is the most suitable and promising material for actuators because it shows low viscoelastic losses. Additionally, **A2** has a low \(T_g\) (–56.8 °C), a low elastic modulus \((Y_{10\%} = 0.54 \text{ MPa})\), high elongation at break (164%), and an increased dielectric permittivity \((\varepsilon' = 5.5 \text{ at } 1\text{kHz})\).
Table 2. Density ($\rho$), glass transition temperature ($T_g$), elastic modulus ($Y_{10\%}$), elongation at break, dielectric permittivity ($\varepsilon'$), dielectric loss ($\varepsilon''$), conductivity $\sigma$, $\varepsilon'$/10%, and dielectric breakdown field ($E_b$) of materials An and VHB foil tested at 1 kHz.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\rho$ [g/cm$^3$]</th>
<th>$T_g$ [°C]</th>
<th>$Y_{10%}$ [MPa]</th>
<th>Elong.</th>
<th>$\varepsilon'$ 1 kHz</th>
<th>$\varepsilon''$ 1kHz</th>
<th>$\sigma$ [S cm$^{-1}$]</th>
<th>$\varepsilon'$/10% [MPa$^{-1}$]</th>
<th>$E_b$ [V/µm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>A0$^a$</td>
<td>-63.0</td>
<td>-</td>
<td>-</td>
<td>6.02</td>
<td>0.021</td>
<td>1.4×10$^{-11}$</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>A1$^b$</td>
<td>0.885</td>
<td>-59.3</td>
<td>0.18 ± 0.01</td>
<td>202 ± 26</td>
<td>5.82</td>
<td>0.062</td>
<td>4.1×10$^{-11}$</td>
<td>32</td>
<td>&gt;15</td>
</tr>
<tr>
<td>A2</td>
<td>0.933</td>
<td>-56.8</td>
<td>0.54 ± 0.05</td>
<td>164 ± 44</td>
<td>5.47</td>
<td>0.060</td>
<td>3.3×10$^{-11}$</td>
<td>10</td>
<td>48</td>
</tr>
<tr>
<td>A3</td>
<td>0.944</td>
<td>-53.6</td>
<td>1.45 ± 0.06</td>
<td>91 ± 33</td>
<td>5.24</td>
<td>0.067</td>
<td>4.5×10$^{-11}$</td>
<td>3.6</td>
<td>60</td>
</tr>
<tr>
<td>A4</td>
<td>0.967</td>
<td>-48.8</td>
<td>3.5 ± 0.1</td>
<td>43 ± 16</td>
<td>5.17</td>
<td>0.053</td>
<td>3.5×10$^{-11}$</td>
<td>1.5</td>
<td>74</td>
</tr>
<tr>
<td>A5</td>
<td>0.994</td>
<td>-34.6</td>
<td>7.84 ± 0.94</td>
<td>22 ± 5</td>
<td>3.43</td>
<td>0.022</td>
<td>1.5×10$^{-12}$</td>
<td>0.4</td>
<td>84</td>
</tr>
<tr>
<td>VHB</td>
<td>-</td>
<td>-32</td>
<td>150</td>
<td>&gt;1000%</td>
<td>4.65</td>
<td></td>
<td>3.5×10$^{-12}$</td>
<td>25</td>
<td></td>
</tr>
</tbody>
</table>

$^a$uncross-linked PANB; $^b$viscoelastic; $^c$the average of three samples is given.

Figure 2. Dielectric breakdown of A2 to A5 (a); lateral actuation strain as a function of an electric field of materials A1 to A4 (b); cyclic actuation strain at 0.5 Hz of A1 to A3 (c); and 50 actuation cycles at 0.5-8 Hz of A2 (electric field of 21 V µm$^{-1}$, prestrained by 7.5%) (d).
The influence of cross-linker amount on dielectric breakdown strength \((E_b)\) was investigated by a Weibull probability plot. \(E_b\) was determined using a similar setup to the one reported in [41 in SI].\(^4\) The voltage was gradually increased by 100 V steps up to breakdown. Weibull probability plot (Figure 2a) was created using Origin software based on ten independent measurements for each sample, where the X-axis type is Log 10 and the Y-axis is double logarithmic reciprocal scale: \(X' = \ln(-\ln(1-X))\). The experimental points for samples A2–A5 are in good agreement with the linear fit, thus following the two-parameters Weibull distribution. A1 is so soft and sticky that it was not possible to handle thin films made of it. Therefore, thicker films were used for characterization. These films, however, did not reach the breakdown at 15 V/µm using the voltage source, which delivers a maximum of 5600 V. Based on the Weibull plot, shape \((\beta)\) and scale \((\eta)\) parameters were determined for each sample. The scale parameter \(\eta\) is showing the voltage at which 63.2% of actuators will fail. This value helps determine the maximum voltage at which the actuator can be exposed. The scale parameter \(\eta\) is increasing by the cross-linker amount used from A2 (tested at 48 V/µm) to A5 (tested at 84 V/µm).

The actuation tests were performed on circular actuators constructed from dielectric elastomer films pre-strained at 7.5 % and carbon black electrodes drawn in a circular form of 8 mm in diameter on both sides. As expected, the lateral actuation increased with the \(\varepsilon'/\gamma_{10\%}\). Because of the small \(\varepsilon'/\gamma_{10\%}\) values, materials A3 and A4 showed a negligible actuation. Material A2 showed a maximum actuation of 3% at 25 V/µm, whereas material A1 showed 12% actuation at an electric field as low as 11.5 V/µm.

Materials A1, A2, and A3 were investigated in cyclic actuation tests at 0.5 Hz (Figure 2c). Because the films had different thicknesses, the electric field in each sample was different. The highest actuation was observed again for sample A1, however, because the material had some viscoelastic
losses, the actuator did not relax back to the initial shape, e.g. about 1% remnant strain was observed. However, the actuation strain was comparable for consecutive cycles. The actuators constructed from materials A2 and A3 recovered the initial shape immediately after the voltage was removed and exhibited stable and reversible actuation. The response of material A2 at frequencies ranging from 0.5 Hz to 8 Hz was demonstrated by cyclic actuation tests. The films were prestrained by 7.5% to minimize the measurement error due to buckling (Figure 2d). For each frequency, 50 actuation cycles were conducted. The actuators responded immediately to the applied voltage and recovered the initial shape after discharging, confirming the excellent elasticity of this material. Even at a frequency of 8 Hz, the actuator immediately recovered its initial shape and no hysteresis between the cycles was observed. A negligible decrease in the measured actuation strain at different frequencies was observed.

Material A2, which showed a fast and reversible actuation strain, was further used to construct stack actuators. The step-by-step process we developed is illustrated in Figure 3. The process can be easily adapted to any shape (see S9-S12). First, a thin dielectric layer was coated on a glass substrate by slot-die coating followed by UV irradiation for ten min to cross-link the films. Thereafter, the solution of the electrode was spray-coated through a shadow mask using an airbrush. After the solvent was removed by drying, the entire process was repeated to produce a five-layer stack. The thickness of the dielectric films in the stacks was 160 µm. The printed stacks were cut and tested regarding the leakage current. The voltage was increased up to 3000 V. From 20 stack actuators tested, 10 survived this test with a leakage current below 33 µA.
Figure 3. Schematic of the process used to manufacture stack dielectric elastomer actuators by slot-die coating the A2 dielectric and spray coating the electrode through a shadow mask. See also Supporting Information for manufacturing stack actuators with different shapes.

Stacks of 50 layers (8 mm stack height) were made by overlapping 10 small stack actuators with five active layers on top of each other (Figure 4). The uniformity of the dielectric and electrode layers was evaluated using an optical microscope and showed rather uniform dielectric layers with a thickness of 160±2 µm (Figure 4).

The electrical connection to the active layers in the stack was made with carbon black, while the connection to the high voltage source was made using two thin aluminum stripes. The stack height was then doubled for every step in the fabrication process. Initially, pairs of 5–layer stacks were
stacked, creating ten-layer stacks. The leakage current for the 5-layer stack (11 actuators tested) was then evaluated at 3000 V and varied between $1.37 \times 10^{-8}$ A to $53 \mu$A (av. $1.04 \times 10^{-5}$ A). In the next step, 20 layers and a 50 layer stack were manufactured. The leakage current at the same voltage increased slightly by increasing the number of active layers. Finally, the 50-layer stack was subjected to 2500 V and gave an actuation strain of $25\pm10 \mu$m, representing about 0.3% relative actuation strain for a stack of 8000 µm height (Figure 4). When the voltage was increased to 3000 V, a negligible increase in actuation was observed for the first two cycles, followed by a decrease, which is presumably due to a small breakdown in the stack. This assumption is further supported by the increase in the leakage current over actuation cycles. Although the dielectric layers in the stack are relatively thick, this is likely not a limitation of the dielectric material and the slot-die coating technique used for manufacturing the stack, but rather due to the electrode material used. Attempts to reduce the dielectric thickness were not successful because the dielectric de-wetted from the electrode, producing inhomogeneous dielectric films. This problem is, however, not faced when thicker films are made. These experiments showed that for achieving functional actuators, we need both a suitable dielectric and an electrode material compatible with the dielectric material and the processing. Future work will address this issue.
Figure 4. A stack actuator consisting of 50 dielectric layers (a), photos of the cross-section view of the printed dielectric/electrode layers in a 50 layers stack (b), and actuation of a 50 layers stack at 2500 and 3000 V (c).

CONCLUSION

In summary, we have demonstrated off-the-shelf nitrile–butadiene rubber that can be fast, on-demand, and under normal atmosphere cross-linked into thin films as a promising material for dielectric elastomer actuators. Additionally, the mechanical properties of the materials can be easily tuned by the amount of cross-linker used, and the dielectric permittivity is higher as compared to VHB and regular silicone elastomers. The material can be easily processed into thin films with a thickness of 160 µm by blade coating and slot-die coating. Furthermore, we showed that stack-actuators with uniform dielectric thickness can be manufactured by slot-die coating the dielectric followed by spray coating the electrode through a shadow mask. Both processes can be used in a fully automated industrial process. The performance of the stack actuators was modest, but it can be improved with a better electrode material. The driving voltage can be reduced by decreasing the thickness of the dielectric film, which the slot-die coating can easily achieve. The process is ready for scale-up and can be used with different combinations of dielectric and electrode materials. Additionally, stacks with different sizes and shapes can be easily manufactured using a different shadow mask. Work in this direction is underway.

Supporting Information. $^1$H NMR spectrum and GPC elugram of the poly(acrylonitrile-co-butadiene), impedance spectroscopy data at different frequencies and temperatures of different
materials, photo of the printed devices (Figure S11), the measured leakage current for the printed rectangular actuators (Figure S12), photos of the stack actuators (Figures S13 and S14).

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**Author Contributions**

M.I. conducted the synthesis and the characterization of all materials. A.V. supervised the printing by slot-die coating. M.I. and T.B. manufactured the stack actuators and characterized them. Y.S. helped with the actuators’ construction and testing. D.M.O. selected the polymer, the cross-linking, and the processing used for the manufacturing. D.M.O., M.I., and T.B. wrote the manuscript with input from all authors. All authors have given approval to the final version of the manuscript.

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