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Chemistry of Materials, 33(9), 3321-3334
https://doi.org/10.1021/acs.chemmater.1c00512

2021-05-11

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**Nanophase-Separation in Immiscible Double-Network Elastomers**
**Induces Synergetic Strengthening, Toughening, and Fatigue-Resistance**

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Table S1. Mechanical properties of DN elastomers and gels.

<table>
<thead>
<tr>
<th></th>
<th>$E$ (MPa)</th>
<th>$\lambda_b$ (mm/mm)</th>
<th>$\sigma_b$ (MPa)</th>
<th>$\lambda_y$ (mm/mm)</th>
<th>$\sigma_y$ (MPa)</th>
<th>$W_b$ (MJ m$^{-3}$)</th>
<th>$T$ (kJ m$^{-2}$)</th>
<th>$\varphi_{1st}$ (vol%)</th>
<th>$T_g$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DN-0 elastomer</td>
<td>0.15</td>
<td>6.0</td>
<td>2.6</td>
<td>-</td>
<td>-</td>
<td>4.8</td>
<td>-</td>
<td>20.4</td>
<td>-34.6</td>
</tr>
<tr>
<td>DN-0.1 elastomer</td>
<td>0.14</td>
<td>8.5</td>
<td>1.6</td>
<td>4.8</td>
<td>1.4</td>
<td>9.5</td>
<td>2.0</td>
<td>4.5</td>
<td>-34.7</td>
</tr>
<tr>
<td>DN-0.5 elastomer</td>
<td>0.43</td>
<td>6.6</td>
<td>2.0</td>
<td>3.5</td>
<td>2.3</td>
<td>8.9</td>
<td>6.2</td>
<td>4.1</td>
<td>-</td>
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<tr>
<td>DN-0.9 elastomer</td>
<td>0.91</td>
<td>9.0</td>
<td>2.8</td>
<td>3.0</td>
<td>3.1</td>
<td>19.5</td>
<td>8.2</td>
<td>2.8</td>
<td>-36.2</td>
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<tr>
<td>DN-1.0 elastomer</td>
<td>1.83</td>
<td>6.4</td>
<td>3.5</td>
<td>3.1</td>
<td>4.3</td>
<td>22.0</td>
<td>10.8</td>
<td>5.1</td>
<td>-33.9</td>
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<tr>
<td>$S_2$N elastomer</td>
<td>0.08</td>
<td>13.2</td>
<td>0.4</td>
<td>-</td>
<td>-</td>
<td>1.9</td>
<td>0.5</td>
<td>-</td>
<td>-35.0</td>
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<tr>
<td>DN-0 gel</td>
<td>0.06</td>
<td>4.8</td>
<td>0.6</td>
<td>-</td>
<td>-</td>
<td>0.6</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>DN-0.1 gel</td>
<td>0.08</td>
<td>4.0</td>
<td>1.0</td>
<td>3.4</td>
<td>1.1</td>
<td>1.4</td>
<td>0.2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>DN-0.5 gel</td>
<td>0.10</td>
<td>3.1</td>
<td>1.4</td>
<td>3.0</td>
<td>1.6</td>
<td>1.1</td>
<td>0.3</td>
<td>-</td>
<td>-</td>
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<tr>
<td>DN-0.9 gel</td>
<td>0.11</td>
<td>3.0</td>
<td>1.4</td>
<td>2.8</td>
<td>1.6</td>
<td>1.2</td>
<td>-</td>
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<td>-</td>
</tr>
<tr>
<td>DN-1.0 gel</td>
<td>0.14</td>
<td>3.0</td>
<td>2.1</td>
<td>3.0</td>
<td>2.1</td>
<td>1.6</td>
<td>0.4</td>
<td>-</td>
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</table>

Young’s modulus ($E$), elongation ratio and nominal stress at yielding ($\lambda_y$ and $\sigma_y$, respectively), elongation ratio, nominal stress and input energy density at break ($\lambda_b$, $\sigma_b$ and $W_b$, respectively), fracture energies characterized by trouser-shaped tearing ($T$) and glass transition temperature ($T_g$) are summarized. The volume ratio of first network in DN elastomer $\varphi_{1st}$ is calculated from $\varphi_{1st} = \left( \frac{h_{1st}}{h_{DN}} \right)^3$, where $h_{1st}$ and $h_{DN}$ are the thickness of dried first network and DN elastomer, respectively.
Figure S1. (A) Swelling comparison of S1N prepared with and without electrolyte component in second monomer solution (4.7 M MEA in organic solvent NMF). S1N-0 and S1N-0.1 represent S1N synthesized without any AMPS and with 10% AMPS in feed monomer concentration, respectively. (B) Digital photo of DN-0.1 elastomer.
Figure S2. SAXS results of DN gels. (A) 2D SAXS patterns and (B) corresponding 1D scattering intensity profiles of DN gels prepared with various $f_{\text{AMPS}}$ molar ratios ranging from 0 to 1.0. No phase-separated structure is formed in these DN-$f_{\text{AMPS}}$ gels.
Figure S3. Domain spacing $d_0$ and $FWHM/q_{peak}$ of DN-$f_{AMPS}$ elastomers plotted as functions of $f_{AMPS}$ molar fraction.
Figure S4. Reswelling of DN-1.0 elastomer in NMF. (A) Two swelling processes and (B) corresponding three-dimensional swelling ratios. Processes (i) and (ii) denote direct swelling of DN-1.0 gel and reswelling of dried DN-1.0 elastomer both in NMF, respectively. (C) Tensile curves of DN-1.0 gels for Processes (i) and (ii). Reswelling ratio and tensile behavior of DN-1.0 elastomer are identical to those of corresponding original DN-1.0 gel, confirming that phase separation does not damage double-network structure.
Figure S5. DSC thermograms of DN elastomers generated at 10 K min$^{-1}$. All DN elastomers show same glass-transition temperature $T_g$ around $-35 \, ^\circ C$, corresponding to glass transition of nonpolar PMEA. The testing sample was pre-equilibrated at $-70 \, ^\circ C$ for 10 min and then was heated at a rate of 10 K/min, and measurement was performed from $-70$ to 160 °C using air as a reference.
Figure S6. Rescaled yielding stretch ratio $\lambda_y \lambda_s$ of DN gels and elastomers plotted as functions of $f_{\text{AMPS}}$. In regimes I and II, DN elastomers did not show any and showed obvious phase separation, respectively.
Figure S7. Comparison of rescaled energy-dissipation behaviors of DN-0.1 elastomer and corresponding gel, as studied by cyclic tensile tests. (A, B) Sequential loading–unloading cycles for DN-0.1 (A) gel and (B) elastomer. (C) Rescaled loading–unloading cycles for DN-0.1 gel and corresponding elastomer. (D–F) Rescaled (D) irreversible dissipation ($W_{\text{irr}}$), (E) reversible hysteresis ($W_{\text{re}}$), and (F) irreversible ratio ($W_{\text{irr}}/W_{\text{total}}$) for DN-0.1 elastomer. For comparison, data for DN-0.1 gel are also shown. The cyclic loading-unloading is performed with a strain rate of 0.14 s$^{-1}$ and without waiting time between cycles.
Figure S8. Comparison of rescaled energy-dissipation behaviors of DN-0.5 elastomer and corresponding gel, as studied by cyclic tensile tests. (A, B) Sequential loading–unloading cycles for DN-0.5 (A) gel and (B) elastomer. (C) Rescaled loading–unloading cycles for DN-0.5 gel and corresponding elastomer. (D–F) Rescaled (D) irreversible dissipation ($W_{\text{irr}}$), (E) reversible hysteresis ($W_{\text{re}}$), and (F) irreversible ratio ($W_{\text{irr}}/W_{\text{total}}$) for DN-0.5 elastomer. For comparison, data for DN-0.5 gel are also shown. The cyclic loading-unloading is performed with a strain rate of 0.14 s$^{-1}$ and without waiting time between cycles.
Figure S9. Crack propagation length $c$ as a function of the number of cycles $N$ with different applied stretch ratio $\lambda_{\text{max}}$ for DN-1.0 and DN-0.1 elastomers. (A) For DN-1.0 elastomer, the crack propagation length $c$ initially increases fast, but crack growth slows down soon to a much slower crack propagation rate with increasing cycle $N$. The average crack propagation rate at steady state $dc/dN$ is the slope of $c$ versus $N$ plot taken after 5000th cycles where the crack propagation reaches steady state. (B) For DN-0.1 elastomer, the crack propagation length $c$ increases at a stable rate from initial stage. At $\lambda_{\text{max}} < 2.38$, the $dc/dN$ is taken after 5000th cycles. At $\lambda_{\text{max}} > 2.38$, $dc/dN$ is taken after 200th cycles.
Figure S10. Experimental set-up and characterizing the energy release rate $G$ for DN-1.0 elastomer. (A) Schematic of the experimental set-up. (B) The loading-unloading curves to $\lambda_{\text{max}}$ with increasing cycle $N$. The curves drop greatly at the beginning of the cycles and reach a steady state after thousands of cycles. (C) The area under the unloading curve shown by the blue hatch represents the elastic strain energy density $W_e(\lambda_{\text{max}})$. (D) Evolution of $W_e(\lambda_{\text{max}})$ and (E) $\sigma_{\text{max}}$ with cycle $N$. The $\lambda_{\text{max}}=1.52$ and 2.04 are shown as examples. The $W_e(\lambda_{\text{max}})$ drops greatly at the beginning cycles and reaches a steady state after 2000 cycles. $W_e(\lambda_{\text{max}})$ at the 5000th cycle is used to estimate the energy release rate $G$ by $G = W_e(\lambda_{\text{max}}) \times H_0$. 
Figure S11. Characterizing the energy release rate $G$ for DN-0.1 elastomer. (A) The loading-unloading curves to $\lambda_{\text{max}}$ with increasing cycle $N$. The curves drop greatly at the beginning of the cycles and reach a steady state after thousands of cycles. (B) The area under the unloading curve shown by the blue hatch represents the elastic strain energy density $W_e(\lambda_{\text{max}})$. (C) Evolution of $W_e(\lambda_{\text{max}})$ and (D) $\sigma_{\text{max}}$ with cycle $N$. The $\lambda_{\text{max}}=1.62$ and 2.73 are taken as examples. The $W_e(\lambda_{\text{max}})$ drops greatly at the beginning cycles and reaches a steady state after 2000 cycles. $W_e(\lambda_{\text{max}})$ at the 5000th cycle is used to estimate the energy release rate $G$ by $G = W_e(\lambda_{\text{max}}) \times H_0$. 