Shape Memory Acrylate Polymers Enabled by Radiation Crosslinking

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CIRMS meeting 2016

April 18th, 2016
Shape Memory Polymers (SMPs)

• Shape memory polymers (SMPs): smart materials which can recover from the temporary shape to the permanent shape upon an external stimulus.

• Two types:
  – Thermoplastic SMP: polyurethane
  – Thermosetting SMP: chemically crosslinked polymers

• SMP manufacturing
  – Thermoplastic SMP: conventional processing
  – Thermosetting SMP: reactive processing
  OR post-manufacturing processing – ionizing radiation
Ionizing radiation

- Two competitive processes during the exposure to radiation
  - Chain scissioning
  - Crosslinking
- Charlesby–Pinner equation

\[ s + s^2 = \frac{p_0}{q_0} + \frac{1}{q_0 \mu_1 d} \]

- \( s \): sol fraction
- \( p_0 \): degradation density
- \( q_0 \): crosslinking density
- \( d \): radiation dose
- \( \mu_1 \): starting molecular weight
Earlier work on radiation on acrylate polymers

- Previously, we have studied several acrylate polymer systems

1. Neat poly(methyl acrylate) (PMA) and its blends with sensitizers (TMPTA and TAIC)

2. PMA copolymers: to study specific targets of radiation crosslinking of acrylates

- Main chain hydrogen
- Side chain α-hydrogen

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<table>
<thead>
<tr>
<th>Acrylate System</th>
<th>Methyl acrylate (MA)</th>
<th>Trimethylolpropane triacrylate (TMPTA)</th>
<th>Triallyl isocyanurate (TAIC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-tert-Butylcyclohexyl acrylate (tBCHA)</td>
<td><img src="image" alt="4-tert-Butylcyclohexyl acrylate" /></td>
<td><img src="image" alt="3% TMPTA" /></td>
<td><img src="image" alt="70% MA + 30% tBCHA" /></td>
</tr>
<tr>
<td>2-Carboxyethyl acrylate (CXEA)</td>
<td><img src="image" alt="2-Carboxyethyl acrylate" /></td>
<td><img src="image" alt="5% TMPTA" /></td>
<td><img src="image" alt="70% MA + 5% tBCHA" /></td>
</tr>
</tbody>
</table>

Figure 1. Gel fraction as a function of radiation dose for PMA blended with increasing concentrations of a) TAIC; b) TMPTA.

Figure 1c. Gel fraction as a function of radiation dose

Voit, W.; Ware, Y.; Gall, K. Polymer 2010, 51(15), pp. 3551–3559
3. MA-IBoA copolymer and PLA:
To study radiation temperature effects

Fig. 2 DMA curves of copolymers of 75% MA and 25% IBoA

Fig. 3 DMA curves of PLA blends

Continuing work

- Acrylate copolymer synthesis

<table>
<thead>
<tr>
<th></th>
<th>BuA</th>
<th>IBoA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample #1 composition (wt%)</td>
<td>25</td>
<td>75</td>
</tr>
<tr>
<td>Sample #2 composition (wt%)</td>
<td>33</td>
<td>67</td>
</tr>
</tbody>
</table>

- E-beam radiation

n-Butyl acrylate (BuA)

Isobornyl acrylate (IBoA)
Thermogravimetric Analysis (TGA)

- No obvious difference in thermal decomposition temperature before and after irradiation.
- Radiation did not change samples’ thermal decomposition temperatures but improved the homogeneity.
- Crosslinking density may be low, if any.
All samples were soaked in chloroform at room temperature for a week. None of the irradiated samples dissolved – all swelled in chloroform. All irradiated samples were lightly crosslinked.

<table>
<thead>
<tr>
<th>Sample composition</th>
<th>Dose (kGy)</th>
<th>Swelling rate in chloroform (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25%BuA-75%IBoA</td>
<td>50</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>2118.52</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>1571.39</td>
</tr>
<tr>
<td>33%BuA-67%IBoA</td>
<td>50</td>
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</tr>
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<td></td>
<td>200</td>
<td>2078.00</td>
</tr>
</tbody>
</table>

*Samples irradiated at 50 kGy: swelled samples difficult to separate out from solvent.*
All irradiated samples showed higher glass transition temperatures.
In DMA, samples irradiated at 50 kGy showed the highest $T_g$

All rubbery modulus of irradiated samples dropped lower than 100 kPa – lightly crosslinked
Conclusion and future work

- BuA-IBoA copolymers were crosslinked when exposed to e-beam radiation at 50, 100, and 200 kGy, and the crosslinking density was low.
- TGA showed no difference in thermal decomposition temperature between unirradiated and irradiated samples.
- DSC showed all irradiated samples have similarly higher $T_g$, while DMA showed samples irradiated at 50 kGy have the highest $T_g$.

- Future work:
  - Investigate the specific targets of radiation crosslinking of BuA-IBoA copolymers.
  - Employ TGA-MS (mass spectroscopy) to study the side groups of irradiated polymers, in order to further investigate how the radiation at 100 and 200 kGy affect the samples’ glass transition temperatures.
2. Voit, W.; Ware, Y.; Gall, K. Polymer 2010, 51(15), pp. 3551–3559