Influence of network density on the strain hardening of PMMA copolymers

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Influence of network density on the strain hardening of PMMA copolymers

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Introduction
The intrinsic toughness of glassy polymers depends on the post-yield behavior, on strain softening and strain hardening. Dependent on the loading condition, the macroscopic response to deformation might be brittle, e.g. for poly(methyl methacrylate) (PMMA) and polystyrene (PS) (Fig. 1). Polycarbonate (PC) is ductile, since it necks in tensile testing. Commercial PMMA always contains some copolymer to reduce unzipping and facilitate processing, e.g. ethyl acrylate (EA). Network density and strain hardening can be influenced by addition of EA.

Materials and methods
PMMA-co-PEA containing 0.5 to 25 wt % EA was provided by Arkema. Dynamic mechanical thermal analysis (DMTA) was used to determine the network density. Uniaxial compression was performed at various temperatures to yield the strain hardening modulus.

Results
By DMTA (Fig. 2), the network density can be calculated from the rubbery modulus $G_N^s$ by $\nu_c = N_A G_N^s / RT$ where $R$ is the molar gas constant, $T$ is the absolute temperature, and $N_A$ is the Avogadro number. The network density decreases upon addition of EA, see Table 1.

Conclusions
Increasing the EA content in PMMA increases the chain mobility and thereby reduces the network density and strain hardening modulus. All copolymers seem to behave identically at a certain temperature below $T_g$, since a universal master curve can be constructed. For optimal toughness, the EA content should be low, since high network density and strain hardening are essential for stable deformation.

References:

Table 1: Properties of PMMA-co-PEA copolymers

<table>
<thead>
<tr>
<th>$M_a$ [kg/mol]</th>
<th>$PDI$</th>
<th>$T_g$ [°C]</th>
<th>$\nu_c$ [10^{-9}]</th>
<th>$G_R$ (20°C) [MPa]</th>
<th>$E_R$ (T - $T_g$) [MPa]</th>
</tr>
</thead>
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<td>SEC</td>
<td>SEC</td>
<td>DMTA</td>
<td>DMTA</td>
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<td>compr.</td>
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<td>EA 0.5</td>
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<td>2.07</td>
<td>132.1</td>
<td>0.85</td>
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<td>0.81</td>
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<td>3.34</td>
<td>86.1</td>
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</tbody>
</table>

Uniaxial compression tests at room temperature show that $G_R$ decreases with increasing EA content, see Fig. 3 and Table 1. Fig. 4a shows that $G_R$ decreases with temperature for all 4 copolymers investigated. The thermal mobility of the chains is dependent on the distance in temperature below $T_g$. Shifting the $G_R$ curves onto a $(T - T_g)$ - axis results into a master curve (Fig. 4b).

Fig. 1: The deformation behavior of PS, PMMA, and PC in a) tension can be predicted from the intrinsic properties as measured in b) compression. All tests are performed at $\dot{\varepsilon} = 10^{-2}$ s^{-1}.

Fig. 2): DMTA results; a) dynamic modulus $E$ and b) tan $\delta$ as a function of temperature. $T_g$ and network density increase with decreasing copolymer content.

Fig. 3): Compressive behavior of PMMA-co-PEA at room temperature at $\dot{\varepsilon} = 10^{-2}$ s^{-1}.

Fig. 4): Strain hardening as a function of a) temperature and b) shifted temperature $(T - T_g)$.

/department of mechanical engineering