Communications to the Editor

Dependence of the Ultimate Tensile Strength of Thermoplastic Elastomers of the Triblock Type on the Molecular Weight between Chain Entanglements of the Central Block

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Triblock copolymers consisting of outer polystyrene blocks (PS) and inner rubbery polybutadiene (PB) or polyisoprene (PIP) blocks are very well-known thermoplastic elastomers (TPEs). Their unique thermomechanical properties are associated with a phase morphology of PS domains dispersed in a continuous rubbery matrix. This physical network of flexible chains combines the mechanical performances of vulcanized rubbers and the straightforward processing of thermoplastics. Accordingly, efforts have been made to improve the properties of either the outer1-5 or inner2,6 blocks.

Substitution of fully (meth)acrylate TPEs for the traditional styrene-diene-based materials is worth considering due to the large range of properties known for poly(meth)acrylates. Previous investigations from this laboratory7-9 and other groups10,11 have however shown that the ultimate mechanical properties for this kind of material, particularly poly(methyl methacrylate) (PMMA)-b-poly(alkyl acrylate)-b-PMMA triblock copolymers (MAM), where alkyl can be 2-ethylhexyl (or iso-octyl),7,8 n-butyl,7,8,11 n-propyl,9 or ethyl,11 are relatively poor when compared to the traditional styrene-diene-based TPEs (Table 1). This issue has been recently addressed by Tong and Jérôme, who pointed out that the molecular weight between chain entanglements (M_e) for poly(alkyl acrylates) is much larger than for polydiene.9

This basic difference is worth being emphasized since M_e for the polydiene block is known to play a very important role in the stress-strain behavior of the

Table 1. Molecular Structure and Mechanical Properties of MAM Triblock Copolymers

<table>
<thead>
<tr>
<th>A of MAM</th>
<th>M_n (×10^-3)</th>
<th>PMMA (wt %)</th>
<th>ultimate tensile strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I1²</td>
<td>20-70-20</td>
<td>36.4</td>
<td>11.5</td>
</tr>
<tr>
<td>I2²</td>
<td>30-140-30</td>
<td>30.0</td>
<td>11.9</td>
</tr>
<tr>
<td>I3²</td>
<td>50-140-50</td>
<td>41.7</td>
<td>11.8</td>
</tr>
<tr>
<td>B1⁵</td>
<td>30-150-30</td>
<td>28.6</td>
<td>15.0</td>
</tr>
<tr>
<td>B2⁵</td>
<td>30-100-30</td>
<td>37.5</td>
<td>15.2</td>
</tr>
<tr>
<td>B3⁵</td>
<td>40-210-40</td>
<td>27.6</td>
<td>15.2</td>
</tr>
<tr>
<td>P1⁵</td>
<td>40-195-40</td>
<td>29.1</td>
<td>17.5</td>
</tr>
<tr>
<td>E1⁵</td>
<td>30-110-30</td>
<td>35.3</td>
<td>23.2</td>
</tr>
<tr>
<td>E2⁵</td>
<td>40-170-40</td>
<td>32.0</td>
<td>23.8</td>
</tr>
</tbody>
</table>

¹ I is poly(iso-octyl acrylate). ² B is poly(n-butyl acrylate). ³ P is poly(n-propyl acrylate). ⁴ E is poly(ethyl acrylate).

In this respect, Holden and Legge12 noted that the slippage of the entangled central blocks could result in an increase of tensile strength by delaying the ductile failure of the polystyrene microdomains. Quirk and Morton13 showed that introducing additional chemical cross-links in the central block, thus preventing the stress distribution in the entangled chain network, resulted in a decrease in tensile strength. Among the models12,14-17 proposed to describe the ABA-type TPEs, the “rubber + filler” model12 and the “chain cross-linking + chain entanglement” model16,17 have been able to account for the tensile behavior of PS-b-PB-b-PS (SIPS)12 and PS-b-PIP-b-PS (SBS)17 triblocks at low strain. Bard and Chung17 have discussed the different models. In a chemically cross-linked elastomer, the total shear modulus G can be modeled by the Langley-Grassley equation:16,18

\[ G = G_C + G_E \]  \hspace{1cm} (1)

where G_C is the contribution from chemical cross-links, and G_E is the contribution from trapped entanglements. Recently, Ver State et al. have shown that G_N² (plateau modulus, G_N² = ρRT/M_e) has a dominant effect on the curemeter torque (M_H), which is the equivalent of the
modulus) for a series of vulcanized elastomers of the same chemical cross-linking density. Indeed, a linear relationship was found between $M_H$ and $G^{\infty}_N$. The authors pointed out that the slope and intercept of the trend line could be related to how entanglements become trapped and the fact that a polymer with negligible $G^{\infty}_N$ would have a modulus only from chemical links. In triblock copolymers of the A-B-A type, the dispersed microdomains have the same role as chemical cross-links. Therefore, Bard and Chung extended eq 1 to TPEs of the triblock type, dispersed microdomains have the same role as chemical cross-linking density. Indeed, a linear modulus) for a series of vulcanized elastomers of the same chemical cross-linking density. The authors pointed out that the slope and intercept of the trend line could be related to how entanglements become trapped and the fact that a polymer with negligible $G^{\infty}_N$ would have a modulus only from chemical links. In triblock copolymers of the A-B-A type, the dispersed microdomains have the same role as chemical cross-links. Therefore, Bard and Chung extended eq 1 to TPEs of the triblock type, dispersed microdomains have the same role as chemical cross-links. Therefore, Bard and Chung extended eq 1 to TPEs of the triblock type, dispersed microdomains have the same role as chemical cross-links. Therefore, Bard and Chung extended eq 1 to TPEs of the triblock type, dispersed microdomains have the same role as chemical cross-links. Therefore, Bard and Chung extended eq 1 to TPEs of the triblock type, dispersed microdomains have the same role as chemical cross-links. Therefore, Bard and Chung extended eq 1 to TPEs of the triblock type, dispersed microdomains have the same role as chemical cross-links. Therefore, Bard and Chung extended eq 1 to TPEs of the triblock type, dispersed microdomains have the same role as chemical cross-links. Therefore, Bard and Chung extended eq 1 to TPEs of the triblock type, dispersed microdomains have the same role as chemical cross-links. Therefore, Bard and Chung extended eq 1 to TPEs of the triblock type, dispersed microdomains have the same role as chemical cross-links. Therefore, Bard and Chung extended eq 1 to TPEs of the triblock type, dispersed microdomains have the same role as chemical cross-links. Therefore, Bard and Chung extended eq 1 to TPEs of the triblock type, dispersed microdomains have the same role as chemical cross-links. Therefore, Bard and Chung extended eq 1 to TPEs of the triblock type, dispersed microdomains have the same role as chemical cross-links. Therefore, Bard and Chung extended eq 1 to TPEs of the triblock type, dispersed microdomains have the same role as chemical cross-links. Therefore, Bard and Chung extended eq 1 to TPEs of the triblock type, dispersed microdomains have the same role as chemical cross-links. Therefore, Bard and Chung extended eq 1 to TPEs of the triblock type, dispersed microdomains have the same role as chemical cross-links. Therefore, Bard and Chung extended eq 1 to TPEs of the triblock type, dispersed microdomains have the same role as chemical cross-links. Therefore, Bard and Chung extended eq 1 to TPEs of the triblock type, dispersed microdomains have the same role as chemical cross-links.
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strength measured for a family of MAM and SIPS

value predicted by eq 7. Partial miscibility between

domains, then \( f_e \) would be dependent on the outer block material.

The ultimate tensile strength measured for a series of MAM triblocks of comparable PMMA content (Table 1) is plotted in Figure 2 against \( 1/M_e \) of the central A block (Table 2). The regression equation expressing this linear relationship is as follows:

\[
F = 9.5 + 1.45 \times 10^5 M_e^{3/2}
\]

The experimental observation of a linear dependence of \( F \) on \( 1/M_e \) not only agrees with eq 9 but also supports the hypothesis that \( f_e \) is independent of the central block and rather typical of the outer block (PMMA in the series under consideration).

Since polystyrene has essentially the same \( T_g \) and modulus as PMMA (the moduli for PMMA and PS being 3200 and 3400 MPa, respectively21), A might be assumed to be the same for triblock TPEs containing PS and PMMA, respectively, as hard microdomains. Within the limits of this hypothesis, the ultimate tensile strength of SIBS (IB being isobutylene) and SIPS (IP being isoprene) containing ca. 30 wt % PS has been calculated from eq 10 with \( M_e = 6100 \) for PIP and 8900 for PIB (Table 2). The calculated values for SIBS and SIPS are 25.7 and 33.2 MPa, respectively, and therefore in very good agreement with the experimental data reported in the scientific literature, i.e., 23–26 MPa for SIBS22,23 and 30 MPa for SIPS.13

When polybutadiene (PB)-containing TPEs are considered, the experimental value of the tensile strength (~30 MPa for SBS containing high 1,4-PB) is far below the value predicted by eq 7. Partial miscibility between PS and PB blocks might be one reason for this observation.13

We conclude that the experimental ultimate tensile strength measured for a family of MAM and SIPS triblock copolymers of comparable hard block contents can be accounted for by a simple model for TPEs which supports a previously proposed deformation mechanism, i.e., slippage of entanglements which delays ductile fracture of rigid microdomains. It is also worth noting that the conclusions of this work, which deals with physically cross-linked rubbers, are in complete agreement with the analysis by Ver Strate and Graessley19 for chemically cross-linked rubbers. The critical role played by the entanglements of the central rubbery block should thus be taken into account in the design of any novel thermoplastic elastomers of the triblock type. Finally, this discussion is not intended to present a new theory of TPE deformation but to report an empirical law that has emerged from our experimental observations.

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References and Notes