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

Jiang-Dong Tong and Robert Jerôme*

Center for Education and Research on Macromolecules (CERM), University of Liège, Sart-Tilman, B6, 4000 Liège, Belgium

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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 outer[1−5] or inner[2,6] 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 laboratory[7−9] and other groups[10,11] 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 isooctyl),[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 polydienes.[9]

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

A of MAM	M_n ($\times 10^{-3}$)	PMMA (wt %)	ultimate tensile strength (MPa)
I1[a]	20−70−20	36.4	11.5
I2[a]	30−140−30	30.0	11.9
I3[a]	50−140−50	41.7	11.8
B1[b]	30−150−30	28.6	15.0
B2[b]	30−100−30	37.5	15.2
B3[b]	40−210−40	27.6	15.2
P1[c]	40−195−40	29.1	17.5
E1[d]	30−110−30	35.3	23.2
E2[d]	40−170−40	32.0	23.8

[a] I is poly(isooctyl acrylate). [b] B is poly(*n*-butyl acrylate). [c] P is poly(*n*-propyl acrylate). [d] E is poly(ethyl acrylate).

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 styrene−diene-based triblock copolymers. In this respect, Holden and Legge[12] 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 Morton[13] 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 models[12,14−17] proposed to describe the ABA-type TPEs, the “rubber + filler” model[12] and the “chain cross-linking + chain entanglement” model[16,17] have been able to account for the tensile behavior of PS-*b*-PIP-*b*-PS (SIPS)[12] and PS-*b*-PB-*b*-PS (SBS)[17] triblocks at low strain. Bard and Chung[17] 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]

$$G = G_C + G_E \tag{1}$$

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 $G°_N$ (plateau modulus, $G°_N = \rho RT/M_e$) has a dominant effect on the curemeter torque (M_H, which is the equivalent of the

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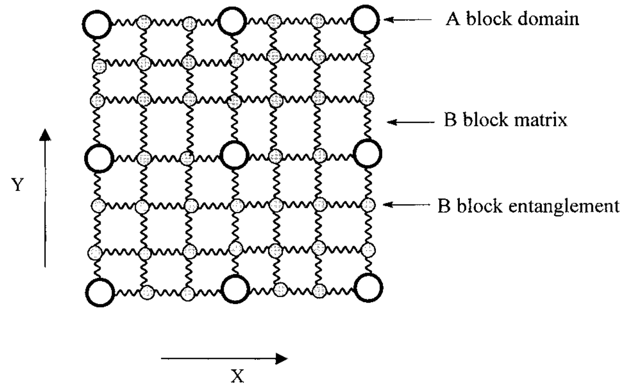

(b)

Figure 1. Cross section of ABA triblock copolymer under tensile test.

modulus) for a series of vulcanized elastomers of the same chemical cross-linking density.[19,20] Indeed, a linear relationship was found between M_H and $G°_N$. 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 $G°_N$ would have a modulus only from chemical links. In triblock copolymers of the A−B−A−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, G_E being however modified in order to account for the role of filler played by the microdomains:

$$G = G_C + T_E G°_N(1/\Phi_B) \qquad (2)$$

where T_E is the Langley trapping factor[18] and $G°_N$ is the plateau modulus for the rubbery block B. The last term in eq 2 accounts for strain amplification in the rubber matrix. Equation 2 gave the best fit for the experimental stress−strain data reported for SBS at low strain. If the contribution of the entanglements is neglected (microdomains acting only as cross-links), then the theoretical predictions are 1 order of magnitude smaller than the experimental data. Nevertheless, in the case of physically cross-linked polymers, e.g., A−B−A−A type TPEs, the influence of the M_e of the central block on the ultimate tensile strength has not been quantitatively discussed yet.

In the ideal case of a fully stretched A−B−A−A triblock under tensile deformation, the force applied must be homogeneously distributed over the whole sample. The sample breaks only when ductile failure occurs in the microdomains of A.[13] In this study, the triblock copolymer is schematized by a cross section of unit area as shown in Figure 1. Figure 1a is the situation when no chain entanglements are formed in the matrix (i.e., very short central block and/or very high M_e). When force is applied, the sample is elongated along the same direction, and the maximum force F that the sample can sustain can be expressed as

$$F = nf_d \qquad (3)$$

where n is the number of hard microdomains (of uniform size) per unit area and f_d is the maximum force sustainable by each microdomain. Compared to Figure 1a, Figure 1b illustrates the case when entanglements are formed by the central block with low M_e. According to the concept of chain entanglements considered in eqs 1 and 2, the applied force must be somehow distributed and shared by the slippage of these entanglements. Assuming that f_d is the maximum force sustained by each microdomain and that f_e is the force shared by the slippage of one chain entanglement, then the maximum applied force F in Figure 1b can be expressed as

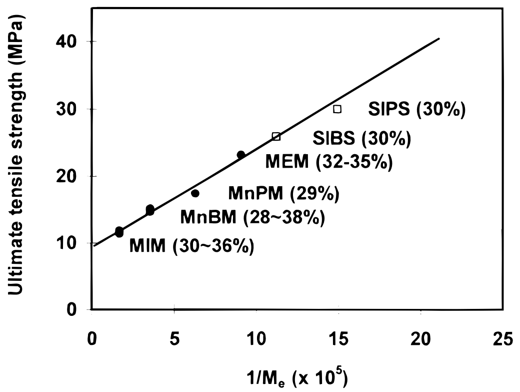

Figure 2. Ultimate tensile strength as a function of $1/M_e$ for MAM triblocks containing ca. 30 wt % PMMA.

$$F = nf_d + mf_e \qquad (4)$$

where m, which is the number of entanglements involved, can be expressed as

$$m \propto m_s p \qquad (5)$$

where m_s is the number of chains in the cross-section and p is the number of entanglements per chain. At constant block copolymer composition, m_s is inversely proportional to M_n:

$$m_s \propto 1/M_n \qquad (6)$$

Furthermore,

$$p = M_n/M_e \qquad (7)$$

where M_n is the molecular weight of the central block. Equation 4 may be rewritten on the basis of eqs 5−7 as

$$F = nf_d + kf_e/M_e \qquad (8)$$

where k is a constant at constant copolymer composition.

It is known that the phase morphology (shape and size of the microdomains) of triblock copolymers is basically dictated by their composition, independent of the molecular weight. Thus, the number of microdomains, n, should be constant at constant composition, and so also should f_d. Indeed, f_d is expected to depend essentially on the nature and size of the microdomains thus on the triblock composition. Equation 8 can accordingly be simplified as follows:

$$F = A + kf_e/M_e \qquad (9)$$

where A is a constant for MAM triblocks of a given composition. Since the cross section in the model is of unit area, F is also the ultimate tensile strength of the triblock copolymer, A being the contribution from the PMMA microdomains and kf_e/M_e from the entanglements.

If the force shared by the slippage of the physical entanglements of the central block, f_e, is controlled by

Table 2. Average Molecular Weight between Chain Entanglements (M_e) for a Series of Polymers

polymer	M_e	polymer	M_e
poly(1,4-butadiene)[12]	1700	poly(*n*-propyl acrylate)[a]	16000
polyisoprene[12]	6100	poly(*n*-butyl acrylate)[a]	28000
polyisobutylene[12]	8900	poly(isooctyl acrylate)[9]	60000
poly(ethyl acrylate)[a]	11000		

[a] Measured by us according to the same technique as reported in ref 9.

the force transmitted at the connection with the microdomains, 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 regressed equation expressing this linear relationship is as follows:

$$F = 9.5 + 1.45 \times 10^5/M_e \qquad (10)$$

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, respectively[21]), *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 SIBS[22,23] 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 Graessley[19] 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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