# Multiphase Elastomeric Networks Prepared from Poly(dimethylsiloxane) and Butadiene–Acrylonitrile Copolymer

Rubbery polymers and copolymers have found wide application in multiphase systems, where they can be used to increase the toughness of both thermoplastics and thermosets.[1-4] They are generally dispersed as small domains in the polymer being reinforced, and function by absorbing impact energy, which might otherwise cause its failure. Two-phase systems in which both polymers are elastomeric are, of course, also known,[5] but have not received nearly as much attention.

The type of elastomer which might most benefit from the presence of a second elastomeric phase would be the noncrystallizable or difficultly crystallizable variety. Such elastomers cannot reinforce themselves by strain-induced crystallization[6] and are therefore inherently weak.[7] Elastomers prepared from poly(dimethylsiloxane) (PDMS) [—Si(CH$_3$)$_2$O—], which has a melting point of $-40°C$,[8] are the most important example of this category.[6] The present investigation therefore focuses on two-phase systems prepared from PDMS and a butadiene–acrylonitrile copolymeric elastomer, which is much used to reinforce epoxy resins.[9] Since toughening effects are being sought, the primary quantities of interest are the ultimate properties of the resulting elastomers, particularly as a function of composition.

EXPERIMENTAL

The sample of PDMS employed consisted of hydroxyl-terminated chains with a number-average molecular weight M_n of 21.3×10^3 g mol^{-1}. The other elastomer was an amine-terminated butadiene–acrylonitrile copolymer (ATBN), commercially available as Hycar 1300X16.[10] It had the structure

$$HN \underset{}{\bigcirc} N(CH_2)_2NHCO[(CH_2CHCHCH_2)_x(CH_2CHCN)_y]_m CONH(CH_2)_2N \underset{}{\bigcirc} NH$$
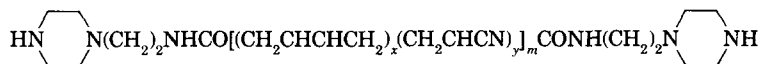
with stereochemically irregular butadiene sequences, $m \simeq 10$, ~ 16.5 wt % acrylonitrile, and $M_n = 3.6 \times 10^3$ g mol^{-1}.[10] These samples were generously provided by the Dow Corning Corp. and the B. F. Goodrich Co. Chemical Group, respectively. The PDMS was mixed with an equivalent amount of the tetrafunctional end-linking agent TEOS [Si(OC$_2$H$_5$)$_4$], and an amount of catalyst, stannous-2-ethyl-hexanoate, corresponding to 3 wt % of the PDMS. Varying amounts of a 20 wt % solution of ATBN in toluene were then mixed into portions of the PDMS–TEOS–catalyst mixture. The resulting mixtures were cloudy-white, presumably because of the immiscibility of the two polymers. They were poured into molds 1.0–1.5 mm deep, and then placed under vacuum for 1 week to remove the toluene solvent and ethanol generated in the PDMS endlinking reaction.[11,12] The compositions thus achieved are listed in the first two columns of Table I. The networks were then placed into 2,4-tolylene diisocyanate (TDI), a liquid, at room temperature for 24 h. The amount of TDI absorbed ranged from 14 wt % in the case of the sample containing 1.23 wt % ATBN to 80 wt % for the sample containing 5.66 wt % ATBN. During the swelling procedure, the NH groups in the ATBN reacted with the isocyanate groups to give a network presumably interpenetrating[13,14] the PDMS network. Each sample was then placed in distilled water for 24 h to neutralize unreacted TDI, and extracted with tetrahydrofuran and then toluene for a total of 6 days.

Strips having the approximate dimensions 1×1.0–1.5×20 mm were cut from each unswollen network sheet and then used in elongation experiments to obtain the stress–strain isotherms at 25°C.[12,15] Preliminary experiments indicated that the multiphase elastomers were sluggish, requiring extended periods of time to approach elastic equilibrium. For this reason, the value of the elastic force f employed was that exhibited 10 min after the strain was imposed.

TABLE I
Network Compositions and Ultimate Properties

Wt % ATBN	Mol % ATBN	α_r[a]	$(f/A^*)_r$[b] (N mm^{-2})	$10^3 E_r$[c] (J mm^{-3})
0.00	0.00	3.15	0.311	0.403
1.23	6.85	3.68	0.715	1.09
1.98	10.7	4.60	1.11	2.06
2.91	15.0	4.25	1.18	1.92
4.31	21.0	4.76	1.59	> 3.29[d]
5.66	26.2	5.45	2.74	> 5.99[d]

[a] Elongation at rupture.
[b] Ultimate strength, as represented by the nominal stress at rupture.
[c] Energy required for rupture.
[d] Samples could not be ruptured with the clamping system available.

was imposed. The elastomeric properties of primary interest are the nominal stress $f^* \equiv f/A^*$ (where A^* is the undeformed cross-sectional area) and the reduced stress or modulus $[f^*] \equiv f^*/(\alpha - \alpha^{-2})$, where $\alpha = L/L_i$ is the elongation or relative length of the sample.[16,17]

RESULTS AND DISCUSSION

The stress–strain isotherms obtained on the PDMS and the two-phase networks were first represented as plots of the modulus against reciprocal elongation, as suggested by the Mooney–Rivlin equation[18,19]
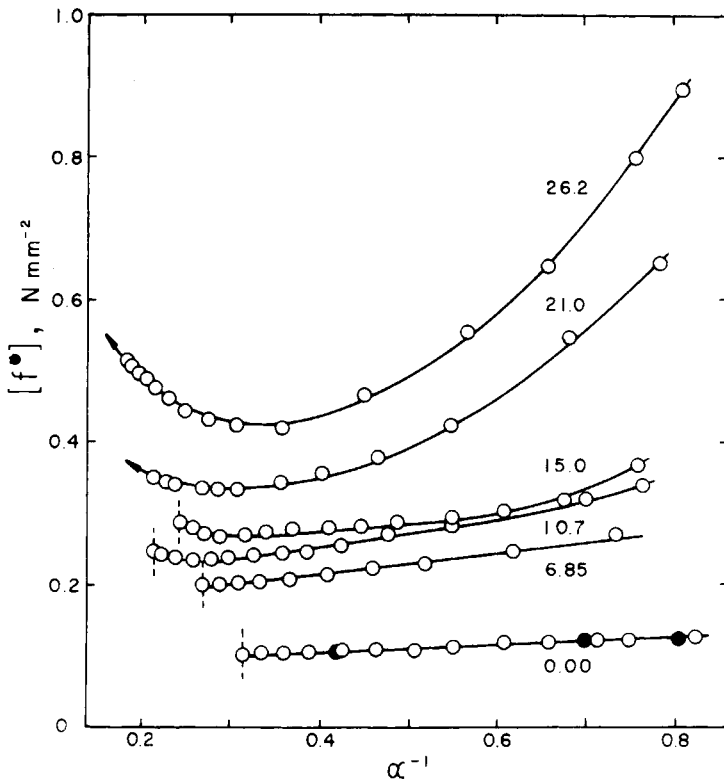

Fig. 1.   The reduced stress or modulus shown as a function of reciprocal elongation at 25°C, with each curve identified by the mol % of ATBN present in the network. In the case of the pure PDMS network (0.00 mol %), the filled circles represents results taken out of sequence to test for reversibility. The vertical dashed lines locate rupture points of the networks.

$$[f^*] = 2C_1 + 2C_2\alpha^{-1} \tag{1}$$

The results are shown in Figure 1. The values of the maximum extensibility obtained from this figure are given in column 3 of the table, with values of the ultimate strength (as represented by the nominal stress at rupture) given in the following column. Figure 2 shows the data of Figure 1 plotted in such a way that the area under each stress–strain curve corresponds to the energy E_r of rupture,[20] which is the standard measure of elastomer toughness. The specific values of E_r are given in the final column of the table, and are shown as a function of composition in Figure 3.

Increasing the proportion of ATBN chains, which are shorter than the PDMS chains, increases the effective degree of crosslinking and thus the modulus. This is, of course, one factor contributing to the increase in toughness with mol % ATBN documented in Figure 3. Much more interesting are the upturns in the modulus, and the fact that the maximum extensibility shows an increase rather than the usual decrease with increase in modulus. In fact, the two networks containing the largest amounts of ATBN were extremely tough and could not be ruptured with the clamping system being used. Since presumably neither the PDMS chains at 25°C nor the ATBN chains at any temperature can undergo strain-induced crystallization, the upturns in $[f^*]$ and f/A^* must be due to the limited extensibility of the short ATBN chains in the network structure.[12,21] Their role in increasing the extensibility of the networks is not known, but could conceivably be associated with the relatively large number of polar isocyanate crosslinks required for the unusually short ATBN chains. In any case, the improvements in ultimate properties achieved are dramatic and could be of considerable commercial importance.
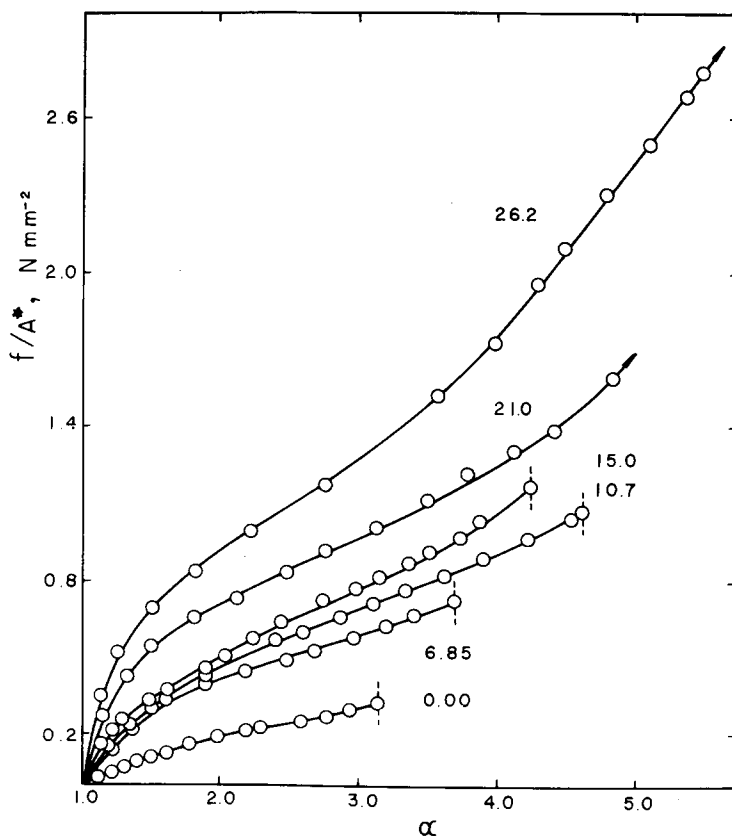

Fig. 2. The results of Figure 1 plotted so that the area under each curve corresponds to the energy E_r of rupture of the sample.
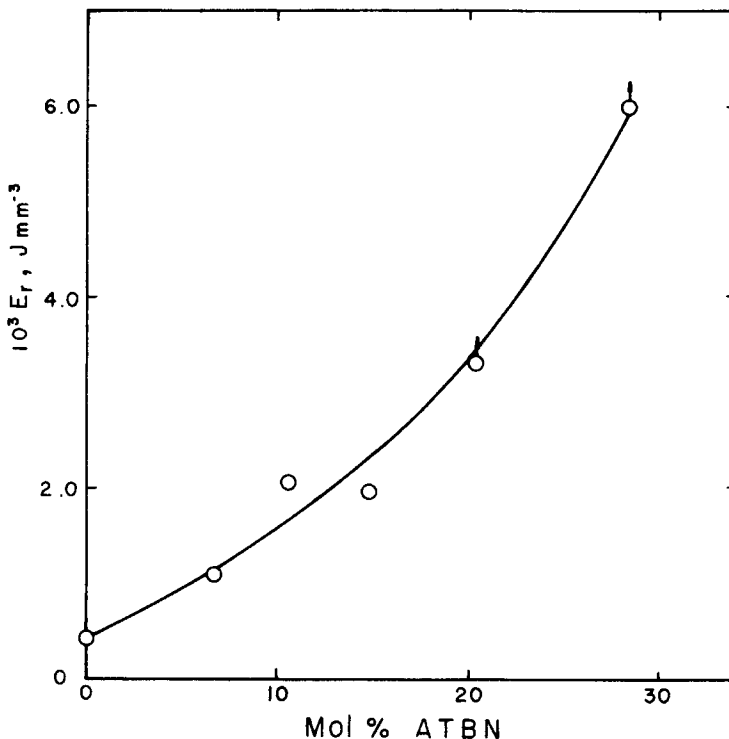
Fig. 3. The dependence of the energy of rupture on the composition of the networks.

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