Chemo-rheological studies of isoprene-butadiene networks

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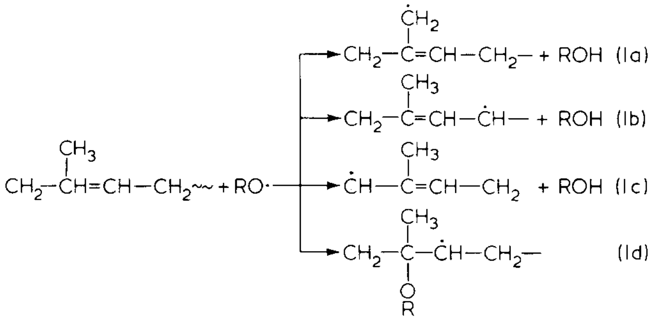
The chemo-rheological behaviour of a systematic series of peroxide-crosslinked butadiene–isoprene block or random copolymers of different architectures (B-I, B-I-B, I-B-I) has been studied. Both intermittent and continuous stress–relaxation experiments in air at 100°C suggest a well-mixed morphology in the copolymers, as evidenced by the systematic increase in the rate of stress relaxation with increasing poly(isoprene) content and by the independence of the chemo-rheological properties of molecular architecture. In general, degradative crosslinking reactions dominate in samples rich in poly(butadiene) while oxidative chain scission controlled the behaviour of poly(isoprene). The copolymers display an interesting balance of these two effects which are primarily dependent on composition.

Keywords Chemo-rheology; isoprene; butadiene; network; peroxide crosslinkages

INTRODUCTION

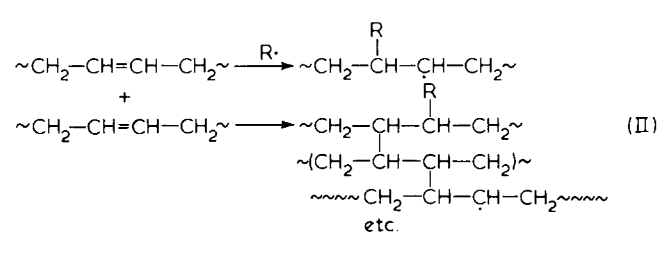
Little information exists that describes the structure property behaviour of block copolymers where both components are in the rubbery state[1]. Most research on block copolymers has been performed on materials where one component is glassy or crystalline at the use temperature and the other is rubbery at the same temperature. Typically, the objective is to produce a thermoplastic elastomer with a hard domain morphology that reinforces the soft matrix and simultaneously provides physical crosslinking. This can be achieved by the synthesis of a block or segmented copolymer where the two components possess a sufficient difference in solubility parameters and are of high enough molecular weight to promote microphase separation. An interesting situation regarding rubber–rubber block or random copolymers is defined by the case where the individual components display opposing chemo-rheological behaviour. For example, suppose one of the blocks is prone to principally degradative chain scission while the other leads to extensive crosslinking. In this case, one might anticipate that with the proper choice of the components, composition ratio, and possibly suitable molecular architecture that these factors could all influence the chemo-rheological behaviour of the system and yield materials with improved properties. Research published on the homopolymers[2–4] has suggested to us that the butadiene–isoprene random copolymers may be such a system.

Tobolsky *et al.*[2] have extensively studied the chemo-rheological behaviour of poly(isoprene) and poly(butadiene) homopolymers vulcanized by various methods. Both natural and many of the synthetic rubbers are particularly susceptible to atmospheric oxidation because they contain reactive allylic C–H and olefinic $-\overset{|}{C}=\overset{|}{C}-$ groups. With regard to this it has been suggested that poly(isoprene) has four sites which are susceptible to attack by alkoxy radicals[5]:



Abstraction of hydrogen predominates here over radical addition.

Poly(butadiene), however, displays quite different behaviour. In addition to possible chain scission reactions, the absence of the methyl group affects the $-\overset{|}{C}-\overset{|}{C}-$ group stability and the material becomes susceptible to extensive crosslinking at the vinyl group; possibly by a chain reaction 'polymerization' step as outlined in equation II [6].



(II)

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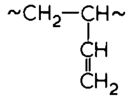
The 1,2 microstructure which is present at the level of ~6% or higher in poly(butadiene) (equation III) is particularly reactive.



$$\sim CH_2-\underset{\substack{| \\ CH \\ \| \\ CH_2}}{CH}\sim$$

III

Oxidative scission at temperatures above 100°C has commonly been studied by continuous and intermittent stress–relaxation experiments[2,7]. The former includes normal stress–relaxation at high temperatures where the material is deformed to a fixed elongation and the stress is followed as a function of time. This procedure provides information on chain scission effects and additional crosslinking due to chemical effects, e.g., peroxides or as shown in Scheme II above. Crosslinks formed by chains severed in the oxidation process are formed after relaxation of the initially stretched chains. Since the new crosslinks are formed from these undeformed chains, they do not contribute to the stress. By contrast, intermittent stress–relaxation involves measuring the stress at a fixed elongation at relatively widely spaced time intervals. Intermittent measurements provide information on chain scission and/or additional crosslinking occurring in the network, including those crosslinks formed from active chains 'cut' during the oxidation process (reversible chain scission). Methods that combine and simultaneously measure both continuous and intermittent effects have been proposed and utilized[8,9]. In general, both continuous and intermittent stress–relaxation experiments together provide insight into the chemo-rheological properties of the polymer system under consideration, as has been well documented by Tobolsky *et al.*[2] and Murakami[7].

Tobolsky demonstrated that both radiation cured *cis*-1,4 and emulsion synthesized polybutadiene polymers displayed a stress increase during intermittent stress–relaxation experiments[10]. Surprisingly, when dicumylperoxide (DCP) was used as a curing agent, the stress decayed steadily during intermittent measurements conducted in air. However, in vacuum the material displayed a rather high degree of crosslinking and the observed stress increased. Murakami *et al.* performed similar experiments using DCP cured *cis*-1,4 polybutadiene (PB–DCP) and *cis* 1,4-polyisoprene (PI–DCP). Their data showed that polybutadiene vulcanizates display a faster stress decay behaviour than polyisoprene at the same temperature. Murakami[7] speculated that there might be weak points near the crosslink sites in PB–DCP which are highly reactive to oxidative chain scission. DCP linking of rubbers involves hydrogen abstraction from the allylic C–H bond and the subsequent formation of polyisoprenyl or polybutadienyl radicals, which are stabilized by allylic resonance as discussed earlier[6].

It has been observed[6] that polybutadienyl radicals are more reactive than the polyisoprenyl counterpart and that direct addition to double bonds by this radical is an alternative route to that of recombination, for the formation of crosslinks (reaction II). Murakami[7] suggested that the allylic hydrogen at the crosslink points in poly(butadiene) are selectively abstracted leading to chain scission near crosslink sites, thus accounting for his data. Our own view regarding Murakami's suggestions is that the behaviour of poly(butadiene) is dominated by crosslinking reactions, although chain scission may still be significant. Radiation curing results in the same type of crosslinks as when peroxide is used. The fact that stress increases in intermittent stress relaxation experiments carried out on radiation cured poly(butadiene) supports the idea of extensive crosslinking occurring in this polymer.

Not all block copolymers display microphase separation. In the case of amorphous polymers, the extent to which phase separation occurs depends on the thermodynamic considerations, which include such features as the molecular weight of the blocks and the degree of block interaction[11]. The differential solubility parameter (Δ), defined as ($\delta 1-\delta 2$) allows a semi-quantitative assessment of the compatibility characteristics of the blocks. The isoprene–butadiene system offers a unique morphological feature since the 'Δ' value is very small (~0.3) and the copolymer might be expected to display a homogeneous morphology up to very high molecular weights. Indeed, Ramos and Cohen[12–15] have reported that the isoprene–butadiene diblock copolymers with 250 000 for a total molecular weight display a homogeneous morphology. Their conclusion is based on the presence of a single T_g from dynamic mechanical and thermomechanical analysis and the successful fitting of the data by use of the Takayanagi model approach. This model relies on temperature composition shifts which in turn depend on additivity of free volume in the individual homopolymers. McGrath *et al.*[16] confirmed and expanded this view since thermal experiments (d.s.c.) showed that diblock samples with molecular weights up to 400 000 were still one phase in agreement with the theory of Meier[11].

Cohen *et al.*[13] showed that polymer blends of poly(butadiene) and poly(isoprene) are incompatible and display a two-phase morphology. It should be emphasized in addition, that it is difficult to characterize possible phase separation in the isoprene–butadiene system by direct techniques such as small angle X-ray scattering due to the small difference in electron densities of the components and hence, little scattering is detected. We believe that our data reported here lends additional support to the conclusions made by Ramos and Cohen, and McGrath and coworkers regarding morphological homogeneity.

EXPERIMENTAL

The polymers used in this study were synthesized by anionic polymerization using sec-butyllithium initiator in hexane solvent[19]. Both polydienes contained over 90% of the 1,4 microstructure as revealed by i.r. spectroscopy (*Table 1*). Dicumyl peroxide (recrystallized) was added to the purified polymers in a 5% polymer solution in hexane. The recovered dry cast films were then compression-moulded at 150°C to induce the peroxide crosslinking reaction. For a fixed peroxide content and fixed crosslink density, it was necessary to cure the films for different times since the efficiency of the crosslinking reaction is composition dependent. Specifically, the samples with high isoprene content required longer curing times than those samples with high poly(butadiene) fractions. The crosslink density was checked by swelling experiments[17] and by utilizing rubber elasticity theory in conjunction with equilibrium stress measurements from stress–relaxation tests carried out at ambient temperature[17]. The

Table 1 Characteristics of the polybutadiene and polyisoprene homo- and copolymer materials used in this study

System		$\langle M_n \rangle$ 10^{-3}	Curing time* (min)	Swelling index (wt. swollen rubber / wt. dry rubber)	M_c† (from stress–relaxation) (g/mol)	Polybutadiene isomers‡ (%)		
						cis 1,4	*trans* 1,4	1,2
BI (Random)	50/50	190	5	2.6	5200	38	54	8
BI (Diblock)	50/50	195	5	2.65	5200	37	57	6
BIB (Triblock)	27.5/45/27.5	225	5	2.65	5200	38	56	6
BIB-50 (Triblock)	25/250/25	211	5	2.71	5400	37	56	7
BIB-86	43/17/43	190	2.3	2.69	5300	37	57	6
BIB-70	35/30/35	202	3.5	2.57	5200	37	56	7
BIB-27	13.5/73/13.5	180	20	2.50	5150	42	62	6
BIB-7	3.5/93/3.5	216	63	2.70	5400	45	50	7
PI (Homopolymer)	–	200	120	2.60	5200	–	–	–
PB (Homopolymer)	–	195	1.5	2.67	5200	–	–	25

* 2% by weight dicumyl peroxide, cured at 150°C

† Stress relaxation at ambient and 50% elongation

‡ I.r. data, not normalized, when this is done,typical values are 40, 53, and 7% for *cis, trans*, 1,2, respectively

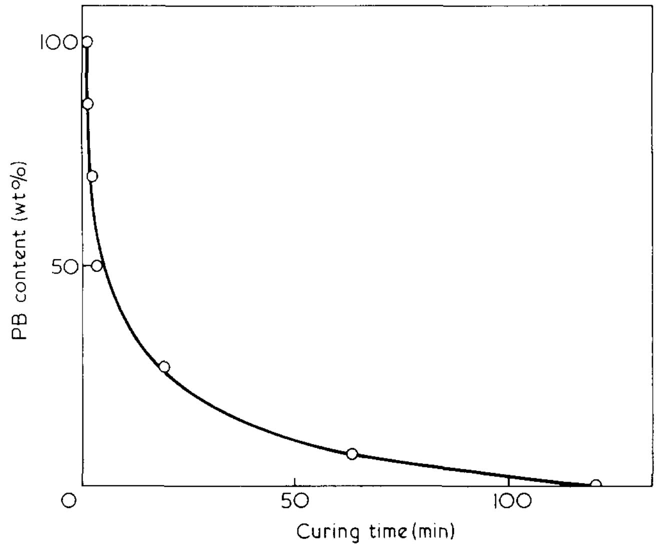


Figure 1 Relationship of polybutadiene content in the copolymer to required crosslinking time at 150°C for an equal degree of crosslinking

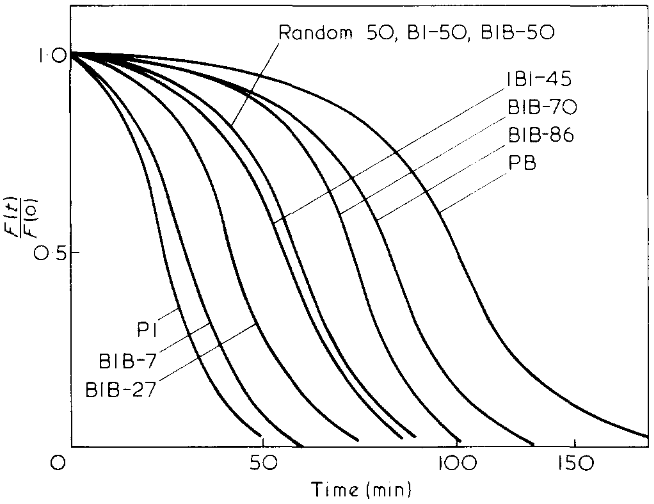


Figure 2 Effect of copolymer structure and architecture on the continuous stress–relaxation of peroxide cured networks poly(butadiene)–poly(isoprene). $\lambda = 1.5$; temperature = 100°C

cured films were extracted in a soxhlet for 24 h in hexane to remove the sol fraction ($\sim 1\%$), and for another 24 h in acetone to extract any remaining peroxide decomposition products.

The stress–relaxation experiments were carried out using a UTM-II Tensilon (Toyo Manf. Co.) in conjunction with an oven and a TC4 proportional temperature controller. All tests were performed in air at 100°C with an elongation rate of 50 mm min^{-1} and a constant elongation of 50%. The dog-bone specimens were 20 × 5 mm and the thickness was 0.25 mm so that diffusion limitations of oxygen were minimized[18]. It took $\sim$30 s for a complete cycle of deformation-recovery to be performed. This time was considered satisfactory in light of the time span of the intermittent experiments.

DISCUSSION

Table 1 summarizes the properties and the characteristics of the homopolymers and copolymers studied. All materials had a value of $\bar{M}_n$ near 200 000 and these were nearly monodisperse as revealed by gel permeation chromatography (g.p.c.). The polymers also contained more than 90% of the 1,4 microstructures except the polybutadiene homopolymer which contained 25% of the 1,2 isomer. *Figure 1* shows the effect of peroxide initiated crosslinking. It is of interest to note that to achieve a swelling index of 2.5 at 2%, by weight of peroxide, curing for only 90 s was required for the poly(butadiene). However, for the same concentration of peroxide 2 h of curing were necessary for the poly(isoprene) to obtain the same degree of crosslinking (as judged by swelling). The high reactivity displayed by the poly(butadiene) sample cannot be attributed solely to the 1,2 structure alone since vulcanization showed a non-linear dependence on composition. For example, the sample with 73% poly(isoprene) (BIB-27) required only 20 min of curing with 2% peroxide to achieve the same swelling index. A plausible explanation for this behaviour is that the efficiency (i.e., kinetic chain length) or the kinetics of the crosslinking reaction depicted in reaction II is very high. Although the mixed morphology of the system might be playing an important role in this behaviour, no conclusive evidence is available on that point to actually correlate the morphological texture of the polymer with its curing behaviour.

Additional information was gained by examining the continuous stress–relaxation data shown in *Figure 2*. Specifically, there is a systematic increase in the stress decay as a function of increasing poly(isoprene) content. However, increasing the poly(butadiene) fraction clearly increases the rate of crosslinking and therefore decreases the stress–decay process. The intermittent experiments

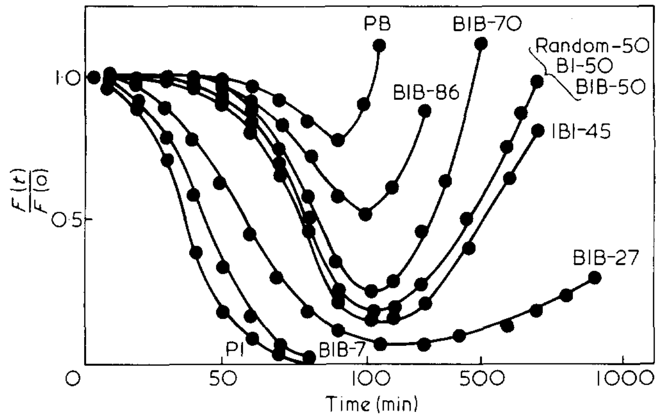


Figure 3 Effect of copolymer structure and architecture on the intermittent stress–relaxation peroxide cured networks of poly)butadiene)–(isoprene). λ = 1.5; temperature = 100°C

offer additional evidence to the conclusions made in the discussion above (see *Figure 3*). In particular, the stress displayed by the poly(butadiene) homopolymer increases with time and almost doubles in value after two hours. In fact, the samples showed a high degree of crosslinking and broke upon extension. The intermittent measurements also show a systematic decrease in the stress growth as the composition changes from pure poly(butadiene) to pure poly(isoprene). For example, the sample with 27% poly(butadiene) displays an interesting behaviour where the stress still shows a dramatic increase with time indicating that the efficiency of the oxidative crosslinking is still rather higher than that of the chain scission process. This behaviour is in contrast to earlier conclusions made by Murakami[7] regarding the stress–relaxation behaviour of *cis* 1,4 poly(isoprene) and *cis* 1,4 poly(butadiene) homopolymers. However, our results are consistent with the observations of many rubber technology studies that show PB systems to harden[3] and PI systems to become tacky. We feel that the behaviour of our polymers and copolymers can be accounted for by three main mechanisms: (1) irreversible chain scission of poly(isoprene); (2) reversible chain scission of poly(butadiene); and/or (3) crosslinking, possibly by 'polymerization' of the poly(butadiene) units. The first of these factors is evident since little difference occurs between the intermittent and continuous stress–relaxation behaviour of poly(isoprene). However, while reversible chain scission has little contribution to the stress behaviour in the continuous experiments since any chains severed and reformed will do so in the relaxed state, the intermittent measurements reveal that this phenomena might be rather extensive in poly(butadiene) and accounts for the high stress displayed by the polymers containing poly(butadiene). However, the stress increase could also be attributed to the crosslinking or the 'polymerization' reaction of poly(butadiene) units (Reaction III), since poly(butadiene) homopolymer and copolymers of poly(butadiene) display a decreased stress–decay behaviour compared to that of pure poly(isoprene). We speculate that the stress increase in these polymers is due to this phenomena and not necessarily due to reversible chain scission.

Figures 2 and *3* also reveal that the 50/50 composition of the random, diblock, and triblock copolymers (Random-50, BI-50, BIB-50, IBI-50) display an interesting behaviour. The stress–decay is found to be independent of the molecular architecture. This observation, along with the systematic decrease in stress–decay with increasing poly(isoprene) content and the crosslinking data in *Figure 1* suggest a homogeneous morphology in accordance with earlier observations[12–16]. That is, one would have anticipated a different behaviour than that displayed in *Figures 2* and *3* if the material was phase separated since the crosslinking and oxidative scission process would have involved selective discrete regions that would be strongly dependent on the morphological texture of the polymer.

CONCLUSIONS

This work emphasizes the novel chemorheological behaviour of isoprene–butadiene copolymers. At relatively high temperatures, there are two competing processes that affect the mechanical property of the copolymers. The first may involve both reversible chain scission and rapid crosslinking while the other is irreversible chain scission. The first of these most important degradative reactions is dominant in poly(butadiene) while the second seems to dominate in poly(isoprene). However, in the block copolymers studied, the behaviour of the samples was dependent on the composition but was independent of the molecular architecture. The systematic behaviour displayed by the polymers suggest well-mixed morphology as has been reported by others, using more conventional methods for miscibility assessment.

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