

Mechanical properties of carboxylato-telechelic polyisoprene

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The mechanical properties of carboxylato-telechelic polyisoprenes neutralized with barium, aluminium and zirconium have been studied. In addition to the variable of neutralizing cation valence, the effect of molecular weight was also investigated. It was found that, for those cations studied, increasing cation valence at an approximately constant molecular weight results in increased stresses during a stress-strain experiment. For the barium-neutralized materials, both modulus and observed stresses increase with molecular weight due to entanglement effects. For the zirconium-neutralized materials, this trend is reversed due to the formation of a more well developed network induced by different chemistry.

(Keywords: mechanical properties; ionomers; carboxylato-telechelic polymers; polyisoprene; elastomers; stress-strain relation)

INTRODUCTION

Much of the more recent work on ionomers has been concerned with those possessing elastomeric character. This focus of attention has been due to the widespread interest in utilizing these materials as thermoplastic elastomers, i.e. elastomers which flow at elevated temperatures yet retain their network structure and elastic nature upon cooling.

Several different types of elastomeric ionomers have been studied to date. Lundberg and coworkers¹⁻⁹ have prepared sulphonated EPDM materials (terpolymers of ethylene, propylene and a non-conjugated diene monomer, typically ethylidene norbornene) and have extensively investigated their properties in both bulk and solution. MacKnight and coworkers have studied the behaviour of polypentenamers containing thioglycolate¹⁰, phosphonate^{11,12} and sulphonate^{13,14} groups. Polyurethane ionomers have been studied by Dieterich, Keberle and Witt¹⁵ and more recently by Cooper and coworkers¹⁶⁻¹⁹.

In all of the materials mentioned above, the ionic groups are distributed randomly along the polymer chain. Since the molecular weight between ionic groups is irregular, the resulting network structure is not well defined. An alternative approach is to prepare telechelic polymers which have ionic groups located *only at the chain ends*, i.e. telechelic ionomers. This well defined chain microstructure leads to a network whose structure is much better defined than those resulting from the traditional ionomers, thus simplifying the task of relating structure to properties. By modifying the flexibility of the chain backbone, the molecular weight, the type of ionic group, the neutralizing ion and the extent of neutralization, one may create model materials possessing a wide range of properties.

Otocka, Hellman and Blyler²⁰ first studied the properties of polybutadiene carrying terminal carboxylate groups. More recently, Wilkes, Kennedy and coworkers have studied the solid-state mechanical²¹⁻²⁵, melt rheological^{26,27} and solution^{28,29} behaviour of sulphonated polyisobutylene telechelic ionomers. Broze, Jérôme, Teyssié and coworkers³⁰⁻⁴² have investigated the structure and properties of carboxylato-telechelic polymers based on polybutadiene and polyisoprene. Their studies have focused on dilute solution viscosity behaviour^{30,33,34,42} as well as viscoelastic behaviour in both bulk^{36,37,40,41} and solution^{35,42}. In this paper we report the results of initial studies concerning the solid-state mechanical properties of carboxylato-telechelic polymers based on polyisoprene.

EXPERIMENTAL

Experimental details about the synthesis and neutralization of carboxylic acid telechelic polyisoprene can be found in previous publications^{33,38}. Carboxylato-telechelic polyisoprenes were anionically prepared with a heterodispersity (\bar{M}_w/\bar{M}_n) lower than 1.2 and mean number of carboxylic acid groups per chain of about 1.95. Neutralizations were carried out in solution by adding stoichiometric amounts of barium methoxide and aluminium isopropoxide under anhydrous conditions. Reactions were driven to completion by distilling off the alcohol product. Neutralization with zirconium was accomplished by adding five times the stoichiometric amount of tetra-n-propoxyzirconium to the solution under non-anhydrous conditions. In fact, in this case an excess of metal alkoxide has to be used and hydrolysed by water in order to promote the desired crosslinking reaction³⁸. The result is not a truly intermolecular ionic

bond, but a carboxylato metal oxhydroxide type of intermolecular bridge. Cast films were carefully dried under vacuum at 50–60°C for several days.

Films of about 0.6 mm thickness for mechanical testing were prepared by compression moulding at 100–120°C. Dog-bone shaped samples, measuring 10 mm in length and 2.55 mm in width, were cut from these films.

Stress-strain experiments were performed on an Instron Model 1122 at room temperature (approximately 25°C). Experiments were conducted at a constant strain rate of 100% min⁻¹ based on the initial sample length, unless stated otherwise.

Long-term stress relaxation experiments were performed on a Tensilon/UTM-II (Toyo Measuring Instruments Co. Ltd) because of the excellent stability of this instrument over long periods of time. Samples were strained to either 10 or 25% at a strain rate of 400% min⁻¹. The decay in stress was monitored for up to 10⁴ min.

Creep experiments were conducted at room temperature by applying a load and monitoring the distance between two gauge marks located within the linear region of the dog-bone sample about 5 mm apart. The distance between the two gauge marks was measured with a cathetometer. To maintain a constant initial stress among samples, a 4 g load was applied to a 20 mil (0.02 inch, 0.05 cm) thick sample and was adjusted appropriately for other sample thicknesses. The creep compliance, $D(t)$, was calculated using the relationship:

$$D(t) = \epsilon/\sigma = \epsilon(A/F_t) = \epsilon(A_0/\lambda F_t) \quad (1)$$

where ϵ is the strain, σ is the engineering stress, A is the instantaneous cross-sectional area, A_0 is the original cross-sectional area, F_t is the true stress and λ is the extension ratio. All creep data were obtained at extension ratios less than 1.20.

RESULTS AND DISCUSSION

The effect of molecular weight on the stress-strain behaviour of the materials neutralized with barium is shown in *Figure 1*. Both the modulus and the stress at constant strain are observed to increase with increasing molecular weight. This behaviour is apparently due to the increase in the number of entanglements per chain as molecular weight increases. This would mean that entanglement effects are more important than ionic effects in this molecular weight range and for Ba as a neutralizing cation. This is a somewhat different conclusion than that reached by Jérôme and Broze⁴¹ based on viscoelastic behaviour of magnesium-neutralized materials. They observed a transition from behaviour dominated by ionic interactions to behaviour dominated by entanglements at $M_n \approx 20\,000$. The storage modulus G' was observed to decrease as M_n was increased from 15 500 to 20 000 to 36 000, and then to increase with further increases in molecular weight. This different behaviour may be due to the basic difference in type of deformation (steady extension vs. dynamic shear) and the difference in cations (barium vs. magnesium) may also play a role.

Figure 2 shows the stress-strain behaviour of the zirconium-neutralized materials. In this case the trend is reversed from that observed for the barium materials in that the lower molecular weight displays a higher

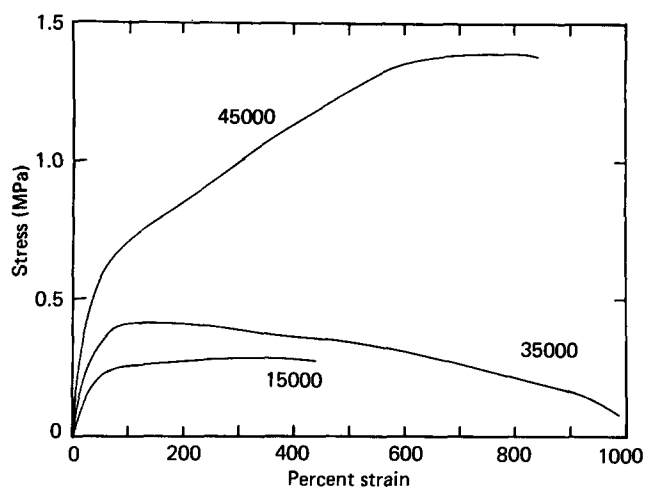


Figure 1 Effect of molecular weight on the stress-strain behaviour of barium-neutralized materials; $\dot{\epsilon} = 100\% \text{ min}^{-1}$; 25°C; M_n values given on curves

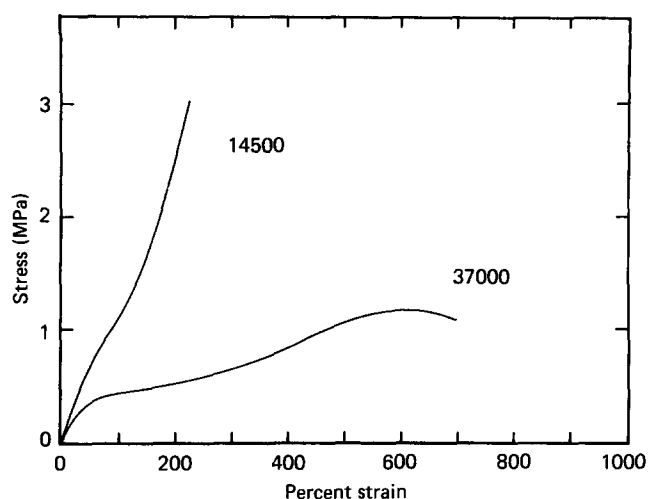


Figure 2 Effect of molecular weight on the stress-strain behaviour of zirconium-neutralized materials; $\dot{\epsilon} = 100\% \text{ min}^{-1}$; 25°C; M_n values given on curves

modulus and higher stress values. The inorganic crosslinks in this material are likely polyfunctional (≥ 3) and the material should thus display a more network-like character than the barium material. A lower molecular weight would lead to a higher crosslink density and thus higher stresses as observed. A similar dependence of stress-strain behaviour upon molecular weight has been observed by Bagrodia *et al.*^{2,3} for sulphonated polyisobutylene telechelic ionomers.

Figure 3 shows the effect of cation valence at an approximately constant molecular weight of 14 500–15 000. For the zirconium- and aluminium-neutralized materials, Young's modulus is approximately the same, while it is substantially lower for the barium-neutralized material. This suggests that the crosslink functionality or crosslink density may be similar for the zirconium and aluminium materials but lower for the barium material. At higher extensions stress decreases in the order $\text{Zr} > \text{Al} > \text{Ba}$. The higher stresses observed for the zirconium material are likely because of the fact that the bonds are more covalent than ionic and are also of higher functionality because of the cation valence and the neutralization pathway. The differences in the behaviour of the carboxy-telechelic polyisoprene end-neutralized

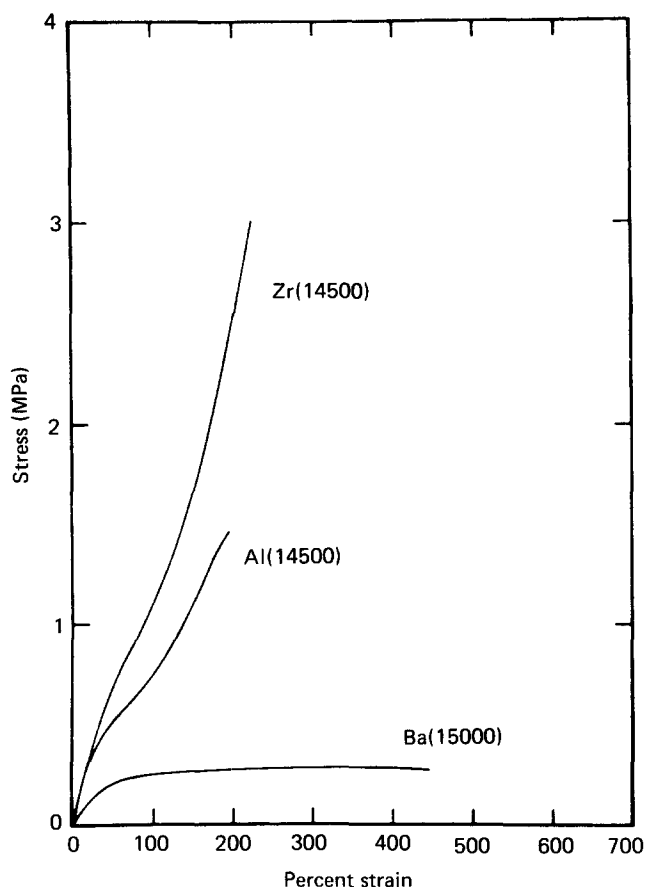


Figure 3 Effect of cation valence on the stress-strain behaviour of materials of $\bar{M}_n = 14\,000$ – $15\,000$: $\dot{\epsilon} = 100\% \text{ min}^{-1}$; 25°C ; \bar{M}_n values given on curves

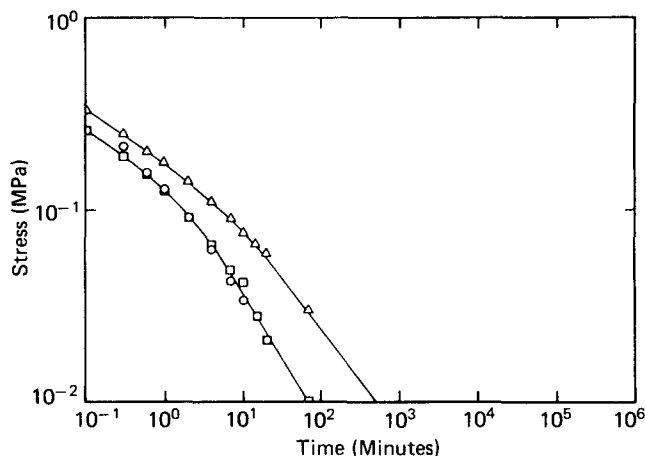


Figure 4 Effect of molecular weight on the stress relaxation behaviour of barium-neutralized materials: $\lambda = 1.25$; 25°C ; \circ , $\bar{M}_n = 15\,000$; \square , $\bar{M}_n = 35\,000$; \triangle , $\bar{M}_n = 45\,000$

with aluminium and barium are apparently due to the differences in cation valence.

Stress relaxation results for the barium and zirconium materials are shown in Figures 4 and 5, respectively. The strains used were 25% for the barium materials and 10% for the zirconium materials, resulting in approximately the same initial stress levels for all of the materials. Although not directly comparable, owing to the difference in strain, certain conclusions can be drawn. The barium materials display a rather rapid decrease in stress, suggesting rather poor network character. The zirconium materials, particularly the $\bar{M}_n = 14\,500$ system, maintain stress levels for a longer period of time, thus indicating a

more permanent network structure. In the case of the barium materials, the relaxation curves for the $\bar{M}_n = 15\,000$ and $35\,000$ materials are essentially identical. For the $\bar{M}_n = 45\,000$ barium material, stresses are significantly higher and the rate of relaxation is somewhat slower. For the two zirconium materials, the relaxation curves appear to be quite different. The initial stress for the $\bar{M}_n = 14\,500$ material is a factor of 2 higher than that for the $\bar{M}_n = 37\,000$ material. The $\bar{M}_n = 37\,000$ material relaxes essentially linearly on this log-log plot while the relaxation curve for the $\bar{M}_n = 14\,500$ material shows two approximately linear regions intersecting at about 1000 min. Relaxation of the $\bar{M}_n = 37\,000$ material is probably primarily due to loss of chain entanglements. Initial relaxation of the $\bar{M}_n = 14\,500$ material may also be primarily due to disruption of entanglements and chain slippage finally giving way to breakage of the zirconium network junctions and flow of the material. Similar stress relaxation behaviour has been observed for sulphonated polyisobutylene telechelic ionomers by Tant and Wilkes⁴³ in which there are two linear regions with the transition also at about 1000 min. However, further studies are needed to clarify the relative importance of each mechanism.

Results of creep experiments for the barium materials are shown in Figure 6. Obviously, the creep rate decreases with increasing molecular weight as would be expected from the stress-strain and stress relaxation behaviour. It is interesting to note that the creep rates for the $\bar{M}_n = 15\,000$ and $35\,000$ materials are quite similar and are greater than that for the $\bar{M}_n = 45\,000$ material. This agrees with the observation that the $\bar{M}_n = 15\,000$ and $35\,000$ materials show almost identical stress relaxation behaviour and relax faster than the $\bar{M}_n = 45\,000$ materials. These results again suggest that molecular weight effects are more important than ion effects in this molecular weight range and for this type of deformation and neutralizing cation.

CONCLUSION

The molecular weight dependence of stress-strain behaviour for carboxylato-telechelic polyisoprene in the range of $\bar{M}_n = 15\,000$ – $45\,000$ is dependent upon the neutralizing cation and the neutralization pathway. For

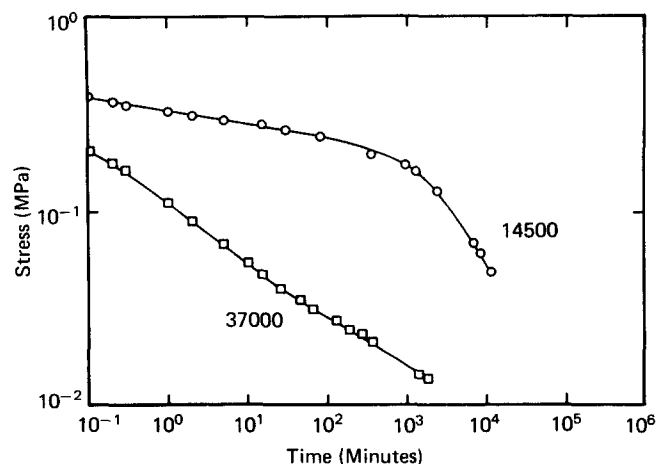


Figure 5 Effect of molecular weight on the stress relaxation behaviour of zirconium-neutralized materials: $\lambda = 1.10$; 25°C ; \bar{M}_n values given on curves

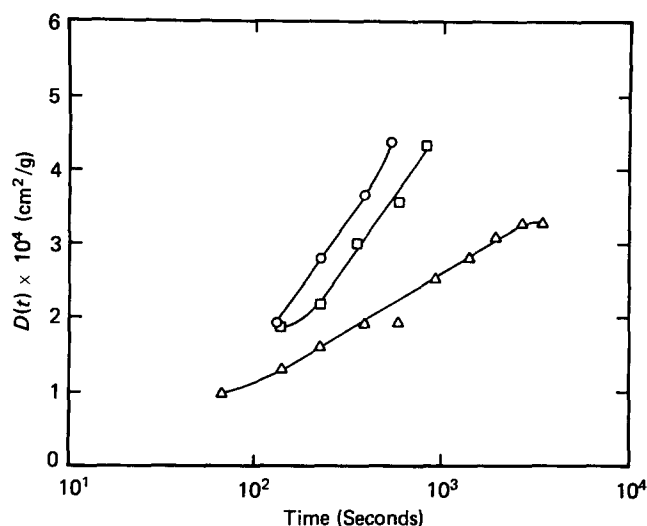


Figure 6 Effect of molecular weight on the creep behaviour of barium-neutralized materials: 25°C; ○, $\bar{M}_n=15\,000$; □, $\bar{M}_n=35\,000$; △, $\bar{M}_n=45\,000$

barium-neutralized materials, modulus and stress increase with increasing \bar{M}_n , indicating the dominance of entanglement effects over ionic effects. This conclusion is supported by creep results in which the creep rate is observed to decrease with increasing molecular weight.

For zirconium-neutralized materials, the reverse trend in stress-strain behaviour is observed, i.e. modulus and stress increase with decreasing molecular weight. This suggests the formation of a more well developed and permanent network induced by the carboxylato metal oxohydroxide intermolecular bridges. Stress relaxation results suggest a similar conclusion. Relaxation of the zirconium-neutralized materials proceeds more slowly than that of the barium-neutralized materials due to the more permanent network.

Cation valence affects the stress-strain behaviour rather strongly. Increasing the cation valence tends to increase the observed stresses for the cations studied.

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