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Hypersonic loss processes in poly(dimethyl siloxane) and the effects of crosslinking

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In an earlier paper we reported Brillouin scattering measurements of the hypersonic sound speed and damping of longitudinal acoustic phonons in a series of poly(dimethyl siloxane) (PDMS) rubbers[1]. It was proposed that the observed dependence of the sound speed (V_s) and loss tangent ($\alpha\lambda_s$) on crosslink density might be accounted for by movement of the α loss peak in a manner analagous to the well-known dependence of the glass transition temperature on the degree of crosslinking.

It was argued that crosslinking the gum extended the minimum size of the region which must simultaneously undergo rearrangement in order to permit mobility — essentially an application of the cooperaitve model of Adam and Gibbs[2]. However, a simple model based on this notion, and assuming the 240K loss peak to be the main α process[3], failed to account quantitatively for the frequency dependence of the loss data. It is the purpose of this communication to report measurements of hypersonic loss in a highly crosslinked PDMS rubber taken over a wide temperature range (200–400K). These measurements were made in order to discover the effect of crosslinking on the 240K loss peak, and in the Figure we display the hypersonic loss tangent ($\alpha\lambda_s$) measured as a function of temperature for a network of shear modulus 6.4×10^5 N m^{-2} (○), and an uncrosslinked fluid of weight-average molecular weight 7.7×10^4 (ICI S273-11-3) (x). Both sets of data were obtained at an internal scattering angle of 124° corresponding to phonon frequencies of ~5 GHz. Experimental technique and sample preparation are discussed elsewhere (see ref 1 and refs therein).

One difference is the method by which our samples are mounted in the light scattering cryostat. It was necessary to freeze the polymer in liquid nitrogen because the smallest traces of vapour prevented the necessary sealing of the small glass vial in which they were held. This difficulty prevented us from obtaining the data presented here at the time of our original work: we found a large and irreversible increase in $\alpha\lambda_s$ in networks handled this way[1]. In this work the samples were held in unsealed cells, and measurements made at the relatively low ambient pressure of the cryostat (~0.1 torr). However, the effects of reducing ambient pressure are not detectable in the Brillouin spectra at room temperature, and we assume any effect to be small over the entire range of temperatures. The fluid data is identical to the 5 GHz data reported elsewhere[4]. Clearly the 240K loss peak is little affected by crosslinking, though the loss maximum may be raised by a few degrees.

A similar small effect is seen on the glass transition temperature in differential scanning calorimetry data[1]. However, the relaxation at ~315K is clearly more sensitive to crosslinking. There is a marked increase in relaxation strength, though experimental uncertainty masks any movement of this loss maximum. We must reject the proposal that the crosslink dependence of the 240K process may account for the observed hypersonic properties of these networks. However, these data do indicate that the 318K process is a main chain relaxation of some sort. Our original assignment of the 240K maximum to the α relaxation was based on an extrapolation of a limited amount of dielectric and microwave data on a transition map[4] and the dominance of this process in determining hypersonic loss in series of PDMS oligomers[3]. However, it may be that both these maxima

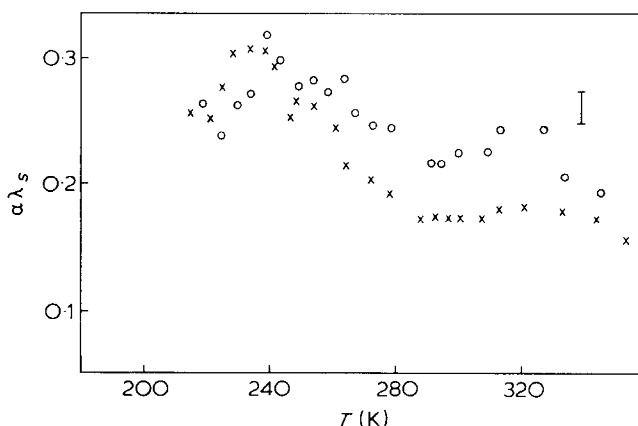

Figure 1 Hypersonic loss tangent ($\alpha\lambda_s$) plotted against temperature for ~5 GHz longitudinal phonons in a PDMS fluid sample (x) and a rubber network of shear modulus 6.4×10^5 N m^{-2} (○). For clarity only one representative error bar is shown

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are associated with the α process in the following manner: The 240K loss process ($R1$) results from a fast chain motion of short correlation length along the chain. The 310K loss process ($R2$) results from a slower motion of longer correlation length at low temperatures. Thus in low frequency dielectric measurements $R2$ dominates and determines the location of the 'α loss' maximum. At higher temperatures the degree of cooperativity required for motion decreases and $R2$ loses strength. However, $R1$ couples strongly to high frequency phonons, thus reversing the relative strengths of the two processes. We are to undertake a careful dielectric study of PDMS at temperatures below T_α to investigate this possibility. Though conjectural in this case, recent work[6] indicates just such a process in poly(4-chlorostyrene). Careful analysis of low frequency (up to a few kHz) data indicates a weak but distinct fast process comprising about 2% of the total dielectric relaxation strength. Plotted on a transition map the fast process data may be extrapolated to meet the point obtained from hypersonic measurements (~ 10 GHz) and assigned to the β relaxation[5], whilst the slower process data indicates that another hypersonic loss maximum may be found at substantially higher temperatures. The 'fast process' data is quite distinct from the so-called β process which occurs at substantially lower temperatures and is characterized by a lower activation energy at these low frequencies. Another difficulty is presented by the relatively strong effect of crosslinking on the hypersonic properties of the rubber even at fairly low crosslink densities[1]. This behaviour contrasts with the small effects seen in model polyurethane networks[7], and it is tempting to account for it in terms of structural scattering (see for example the data of Bedborough and Jackson[8]) associated with crosslink induced structure. However, the similarity of the strength of the 240K process in the fluid and network would seem to preclude this explanation. However, our rubber samples were prepared by radiation crosslinking, and undoubtedly contain small bubbles which may induce local structure[9]. There is also some evidence for a significant number of short chain lengths in these networks[10]. Their presence might influence the hypersonic loss data considerably. Model networks of PDMS are now available[11] and experiments with these materials may clarify the origin of the hypersonic loss we observe at low crosslink densities[1].

In conclusion we report these measurements not only because they confirm our suspicions about the inadequacy of our original model, but also because they cast doubt on earlier rather simple interpretations of the hypersonic loss process. We await the outcome of the experiments referred to for further clarification.

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Electron resists prepared from colloidal dispersions of poly(methyl methacrylate) in non-solvents

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Introduction

Electron-beam lithography has become an important technique in the fabrication of microelectronic devices[1,2]. Its use stems from the fact that it can produce line widths which are an order of magnitude smaller than those available from the best photolithographic processes. Poly(methyl methacrylate), (PMMA), has been widely used as a resist in electron-beam lithography[3,4]. The substrate to be pattern-delineated is usually first covered with a polymer film by spin-coating PMMA from a molecular solution in a good solvent. The system is selectively irradiated by a focused beam of electrons and in what amounts to a developing process the degraded polymer is removed with the aid of a selective solvent to form a positive image. The usefulness of a polymer as a resist depends on its film forming and adhesive properties, sensitivity to electron irradiation, resolution and chemical resistance to etching solutions. Sensitivity for a given film thickness is usually defined as the minimum electrical charge per unit area of resist film required for complete development of the exposed area. Resolution is usually given as the minimum linewidth that can be developed in the resist layer; it is very much dependent on the resist thickness, the line spacing, the accelerating voltage and the nature of the substrate[5]. There are a number of polymers, e.g. poly(butene-1-sulphone), which are considerably more sensitive as electron resist than PMMA[6]. The latter is still extensively used, however, in fabrication

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