

Dynamic Mechanical Studies of Four Elastomeric Fibers at Low, Intermediate, and High Extensions

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Synopsis

A dynamic mechanical study of four elastomeric threads has been made: the threads comprise natural rubber, nitrile rubber, Lycra, and Spanzelle. The dynamic loss modulus (E'') and the dynamic storage modulus (E') were studied over a wide range of temperature (-110°C to 180°C) and the transitions were interpreted in the light of the chemical composition of the materials. The threads were investigated at 2%, 200%, and 400% static strain at a frequency of 110 Hz.

INTRODUCTION

The cyclic deformation of elastomeric threads at zero and very low static strain has little practical significance, as these materials, particularly in their textile application, are most commonly used in a considerably extended form. Elastomeric threads are often subjected to repeated loading and unloading cycles. The object of this work was to examine the behavior of the dynamic loss modulus (E'') and the dynamic storage modulus (E') of natural and nitrile rubber threads and two commercially important polyurethane threads, Lycra and Spanzelle, over a wide range of applied strain.

Mason¹⁻⁴ has reported results for similar investigations of various rubbers. He has studied¹ the complex modulus of a natural rubber vulcanizate as a function of strain up to 600% extension. The real and imaginary components (E' and E'') varied with strain in the same way as the modulus from static experiments. That is, up to around 140% extension, the behavior obeyed a Mooney-type stored energy function, and at higher extensions, it was governed by the finite extensibility of the polymer network. The same author has reported² values of the components of the complex modulus for natural, butyl, and nitrile rubbers from studies of the velocity and attenuation of longitudinal waves in filaments under extensions up to 100% and at 10^3 Hz. Similar studies³ of the real and imaginary parts of the complex modulus of natural rubber con-

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taining 18% by volume of carbon black were made at strains up to 80% and over a temperature range of -30°C to $+30^{\circ}\text{C}$. The moduli showed an increase as a result of the additive, but the glass transition temperature, T_g , was not markedly influenced. Natural and butyl rubbers at extensions up to around 700% have been studied⁴ in the temperature range -45°C to 50°C and over the frequency range of 2×10^2 Hz to 2×10^4 Hz, revealing that at constant temperature and frequency E' and E'' increase with increasing applied strain. The loss factor ($\tan \delta = E''/E'$) decreased with increasing strain, this being more pronounced in the case of the butyl rubber. The relaxation spectra were shifted in the direction of longer time by increasing the strain. This shift was more marked for the natural rubber.

Nolle⁵ has reviewed the knowledge existing up to 1950 concerning the dynamic mechanical properties of rubber-like materials.

It is now generally accepted that polyurethanes show three peaks^{6,7,8} in their mechanical dispersion. These occur over a very wide range of temperature. The molecular origin of these peaks has been the object of some study.^{9,10} In broad general terms, they have been ascribed to the following molecular mechanisms, the details of which have, however, not been resolved. The low-temperature transition which occurs around -130°C has been attributed by Schatzki¹¹ to a rocking motion of methylene sequences. The intermediate transition occurring around -70°C ^{6,7} is reported as only being present when water or some other hydrogen bond-forming low molecular weight substance is present in the polymer. The third transition which can occur over a range of temperature is generally associated with glass-rubber transition. It has become customary to label these three transitions as the α , β , and γ transitions in order of decreasing temperature.

The modulus-temperature behavior of most polymeric systems can be classified into two general types. A rubbery polymer which has not been crosslinked and is not partially crystalline will exhibit a modulus-temperature curve which has a plateau region at very low temperatures followed by a very dramatic modulus drop (about a 1000-fold) at relatively low temperatures which corresponds to the glass transition. This is followed by a rubbery plateau region (10^5 - 10^6 N m⁻²) which is sensitive to molecular weight and which can be extended to higher temperatures by crosslinking. Finally, there is another catastrophic drop in modulus resulting from the onset of flow. Semicrystalline polymers generally have a very high plateau modulus above the glass transition temperature and are generally tough and pliable. The glass transition also produces a dramatic drop in modulus in this case.

Elastomeric polyurethanes can show an uncommonly high rubbery plateau modulus which cannot be accounted for by crystallinity or crosslinking through primary valence bonds. This reinforcement has been attributed to hydrogen bonding and to the possibility of the separation of the hard and soft segments of the polyurethane into domains. These structural concepts are now well documented.¹²⁻¹⁴

EXPERIMENTAL

Materials

Pirflex. A sample of Pirflex nitrile rubber thread having a rubber count of 80 (rubber count is defined as the number of filaments which, when laid side by side, measure 1 in. across) was supplied by United Latex Limited, Melton Mowbray, Leicestershire, England. This thread was manufactured from a copolymer latex containing 63% butadiene, 35% acrylonitrile, and 2% methacrylic acid. The latex was stabilized with potassium oleate and thickened with a styrene-maleic anhydride copolymer. The thread was processed in a manner similar to that of natural rubber latex extruded thread. The acrylonitrile level is quite high, as this usually lies in the range 18% to 40% for nitrile rubbers.

Natural Rubber. A sample of a typical natural rubber thread in current use was kindly provided by Globe Elastic Thread Company Limited, Tiverton, Devon, England. It was a 60 rubber count white thread. It consisted wholly of natural rubber extruded from natural rubber latex, apart, of course, from titanium dioxide for whitening, an antioxidant, and a curing system.

Lycra. Lycra is a polyurethane elastomeric fiber with polyether-based soft segments. The sample used was Type 124 Lycra of 1120 denier, supplied by du Pont (United Kingdom) Limited, Londonderry, Northern Ireland.

Spanzelle. The sample of Spanzelle elastomeric fiber of 1120 denier was supplied by Courtaulds Limited, Coventry, England. Spanzelle is also a polyurethane, but, unlike Lycra, has polyester rather than polyether soft segments.

Methods

Dynamic Mechanical Measurements. All dynamic mechanical measurements were carried out using a Model DDV II Rheovibron Dynamic Viscoelastometer (Toyo Measuring Instrument Company, Tokyo, Japan). The samples were studied over a temperature range from about -110°C to $+180^{\circ}\text{C}$ where this provided to be practical. The samples were heated at a rate of $1-1.5^{\circ}\text{C}$ per min. Most of the measurements were made at a frequency of 110 Hz, but the materials were also studied at 11 and 3.5 Hz. The samples were strained to the desired level and left for 20 min to relax prior to measurement.

Area Determination. Both rubber threads had a circular cross section which allowed the diameter to be measured directly using a microscope fitted with a filar eyepiece. The polyurethane fibers had irregularly shaped cross sections, so for these fibers areas were calculated from density and linear density (mass per unit length). Densities were measured in a xylene-carbon tetrachloride density gradient column maintained at $20 \pm 0.01^{\circ}\text{C}$ (Lycra 1.134 and Spanzelle 1.252 g cm^{-3}).

The area of cross section was required for the calculation of the dynamic moduli from the instrument readings. There is a considerable reduction in area of cross section at 200% and 400% extension. This is allowed for in the calculated moduli at these extensions by assuming no change in volume on extension so that the correction at 200% extension is made by dividing the area of the unstretched specimen by 3 and, similarly, at 400% extension, dividing by 5. No correction has been made for any change in area of cross section with temperature.

Sample History. The samples used were in the as received condition prior to the commencement of dynamic straining. Where more than one filament was required to give an adequate sample, a bundle of threads was attached to tabs using an adhesive (Araldite). The adhesive was set by placing the sample in an oven at approximately 50°C for about 1½ hr. The presence of the adhesive and the act of heating to 50°C had no effect on the $\tan \delta$ temperature dispersion.

RESULTS AND DISCUSSION

Rubber and Pirflex

Figures 1 and 2 show how dynamic storage modulus (E') varies as a function of temperature for the rubbers at 2%, 200%, and 400% strains, respectively. Figures 3 and 4 show the corresponding changes in the dynamic loss modulus (E'').

E' and E'' increased in magnitude for both rubbers at a given temperature as the static strain was increased. This is in agreement with the findings of Mason⁴ for natural rubber, but he found for butyl rubber up to extension ratios of around 6 that E'' , but not E' , was insensitive to strain.

Both rubbers show dynamic loss modulus temperature dispersions dominated by the glass transition which is clearly the only major transition occurring over the temperature range studied, but in both cases there is evidence for other minor transitions. The natural rubber thread showed the greater difference between the maximum and minimum values of E'' over this temperature range, at all three strain levels investigated. The glass transition for natural rubber occurred at a markedly lower temperature than for the nitrile rubber. Table I lists the temperatures at which the major peaks occur for these three levels of static strain. It is clear from the loss modulus data that for natural rubber the glass transition temperature is not markedly influenced by strains up to 400%, but for the nitrile rubber there is a significant shift to higher temperatures occurring between 200% and 400% extension.

Gee, Hartley, Herbert, and Lanceley¹⁶ have shown under conditions of constant stress that the glass transition temperature of natural rubber increased by as much as 7.6°C at 260% strain; but when the specimens were allowed to relax in the glassy state, the effect was reversed. However, Mason⁴ has reported a change not exceeding $\pm 4^\circ\text{C}$ for the glass transition temperature of natural rubber up to 600% extension. He has

TABLE I
Transition Temperatures from Loss Modulus/Temperature Curves at 110 Hz

Sample	Transition	Temp., °C		
		2% Strain	200% Strain	400% Strain
Rubber	β	-53	-54	-53
Pirflex	β	-12	-14	-7
Lycra	β	-68	-62	-61
Lycra	γ	-130	-145	-145
Spanzelle	β	-28	-21	-17
Spanzelle	γ	-90	-85	-90

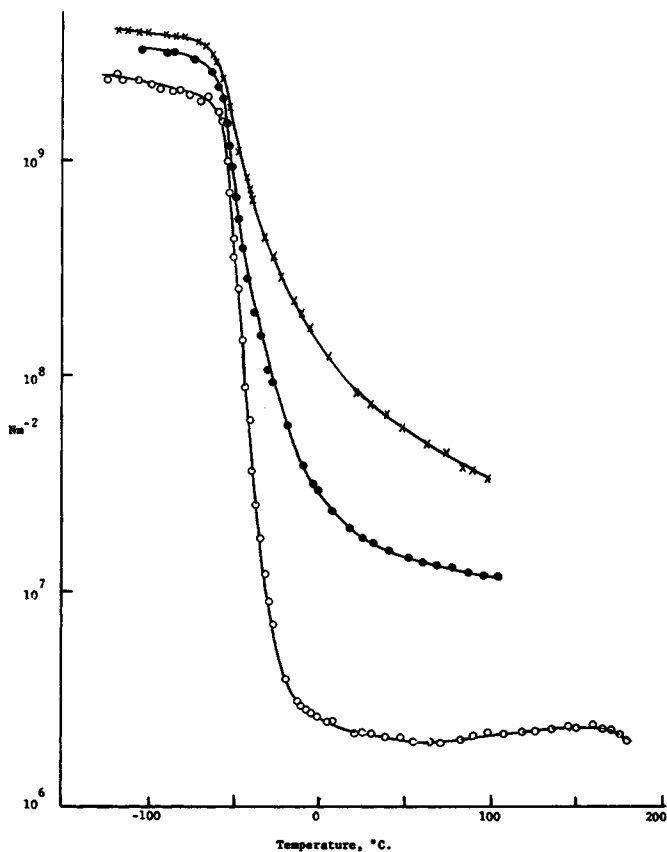


Fig. 1. Storage modulus (E') vs. temperature for natural rubber at 110 Hz and 2% (O), 200% (●) and 400% (×) static strain.

further reported² changes in the glass transition temperatures of $+2^{\circ}\text{C}$ for natural rubber, -2.5°C for butyl rubber, and -1.5°C for nitrile rubber for extensions up to 100%. This latter trend is also shown (see Table I) by the nitrile rubber sample used in this work, but is reversed at the highest strain. In general, the influence of extension on the transition tem-

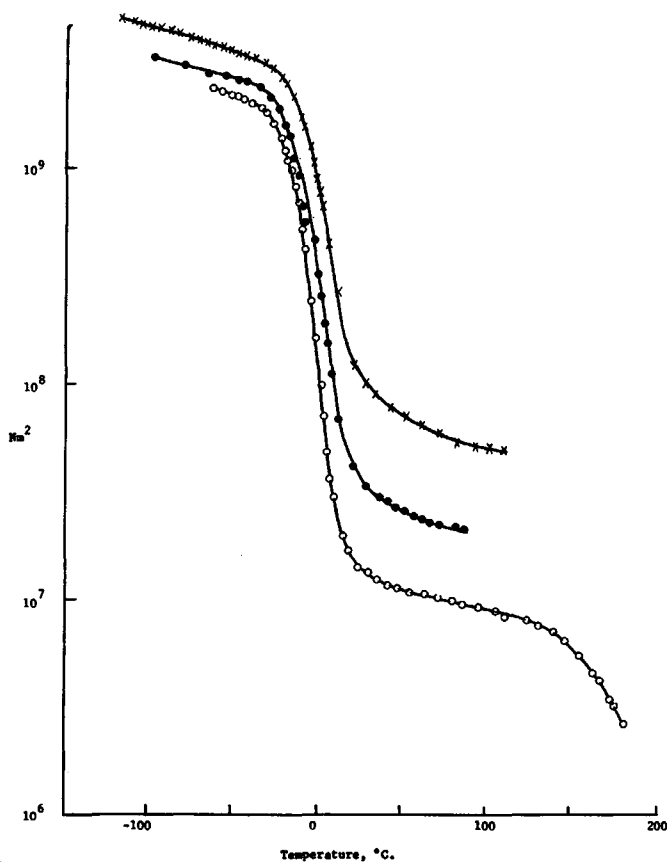


Fig. 2. Storage modulus (E') vs. temperature for Pirflex at 110 Hz and 2% (O), 200% (●) and 400% (X) static strain.

perature may be considered to be twofold. Firstly, there is a stress effect resulting from the increased free volume which is produced by the isotropic part of the stress¹⁶ which results in a lowering of the glass transition temperature; and secondly, there is a strain effect resulting from the enforced change in molecular orientation.¹⁷ This may increase or decrease the glass transition by easing or hindering group rotation. The initial decrease in the glass transition temperature of the nitrile rubber may be due to such an easing of rotation of possibly the nitrile groups.

Evidence about the relative crystallinities of the two rubbers may be inferred from Figures 1 and 2. In Figure 2, the shapes of the nitrile rubber curves at 2% and 400% extension are similar, both being typical of an amorphous polymer. Natural rubber, on the other hand, showed a broadening of the transition region, and at 400% static strain (Fig. 1) showed at least incipient semicrystalline behavior.

Earlier it was mentioned that Figures 3 and 4 showed evidence of other minor transitions. For the nitrile rubber there are two such transitions.

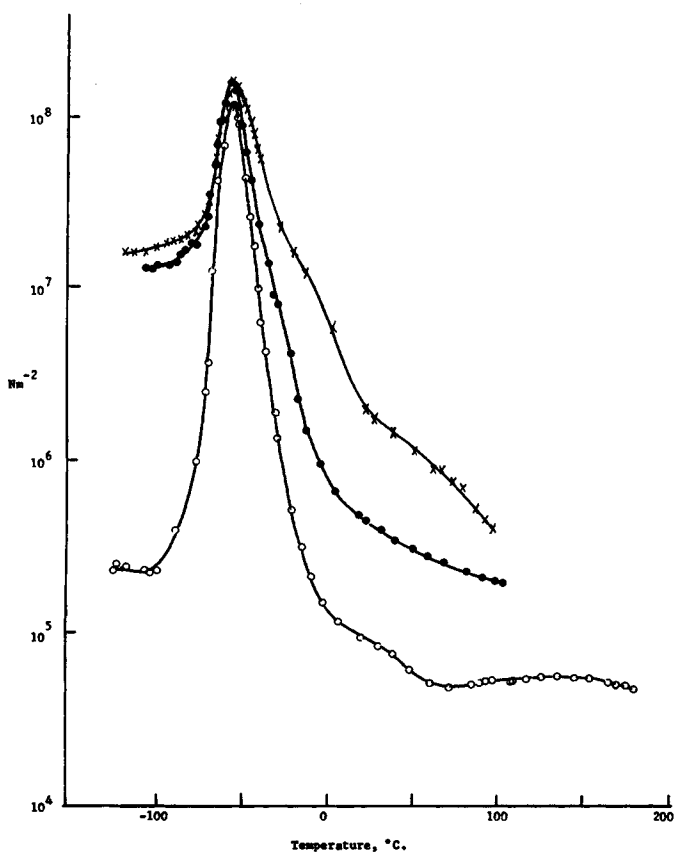


Fig. 3. Loss modulus (E'') vs. temperature for natural rubber at 110 Hz and 2% (○), 200% (●) and 400% (×) static strain.

In the extreme low temperature region, there is a broad transition with no distinct maximum.

The nitrile rubber sample was very brittle at low temperatures and was inclined to break. A transition in this region occurs^{9,10} in polyurethane elastomers and is commonly ascribed to motion of methylene sequences. This cannot be assumed here, as rotation of the nitrile groups is also a possible mechanism. In Figure 4, the nitrile rubber extended 2% shows a small, but distinct transition at around 130°C. Polyacrylonitrile is known to have a transition in this temperature region,¹⁸ so this peak is likely to be caused by blocks of acrylonitrile units of sufficient size to be able to manifest themselves independently.

With natural rubber, the minor transitions are not so marked, but at the highest strain there are two shoulders on the high-temperature side of the major transition (see Fig. 3).

For a copolymer, the following relation has been suggested:¹⁹

$$1/T_g = W_1/T_{g1} + W_2/T_{g2} \quad (1)$$

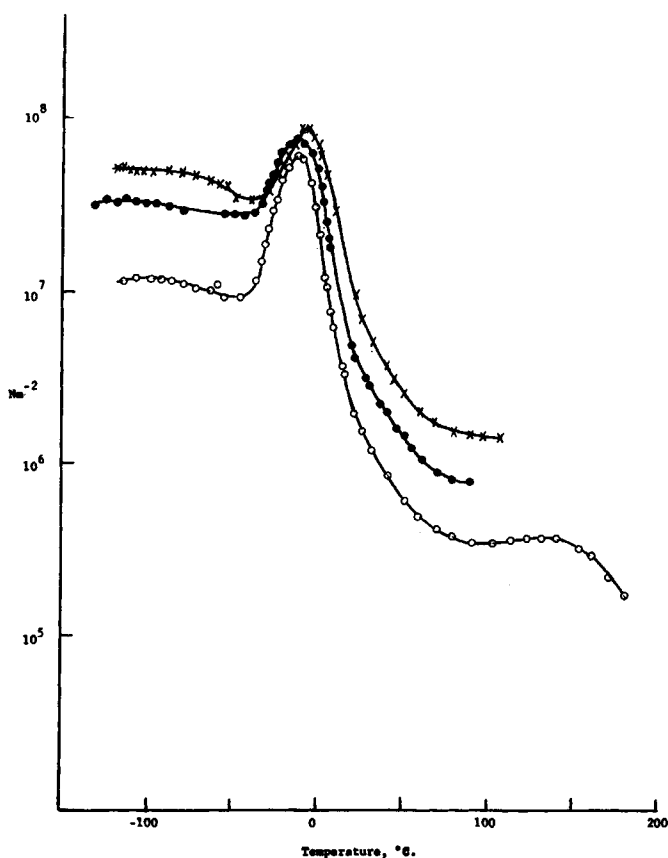


Fig. 4. Loss modulus (E'') vs. temperature for Pirflex at 110 Hz and 2% (O), 200% (●) and 400% (X) static strain.

where T_g is the glass transition temperature ($^{\circ}\text{K}$) of the copolymer, T_{g_1} and T_{g_2} are glass transition temperatures ($^{\circ}\text{K}$) of the homopolymers formed from each comonomer, and W_1 and W_2 are the weight fractions of the respective monomers. However, the glass transition temperature is sensitive to the frequency at which it is measured and, for this reason, the glass transition temperatures used in eq. (1) should be those for polybutadiene and polyacrylonitrile at 110 Hz, but these values are not available. Thus, T_g values for these polymers determined by specific volume changes have to be used. A value of 98°C has been reported²⁰ for the glass transition temperature of polyacrylonitrile, but it is dependent on the degree of crystallinity and molecular weight.²¹ For polybutadiene, this value is highly dependent on the method of preparation.²²

Equation (2) has been suggested²³ for this type of copolymer, where A is the weight per cent of polyacrylonitrile:

$$T_g = -85 + 1.4A. \quad (2)$$

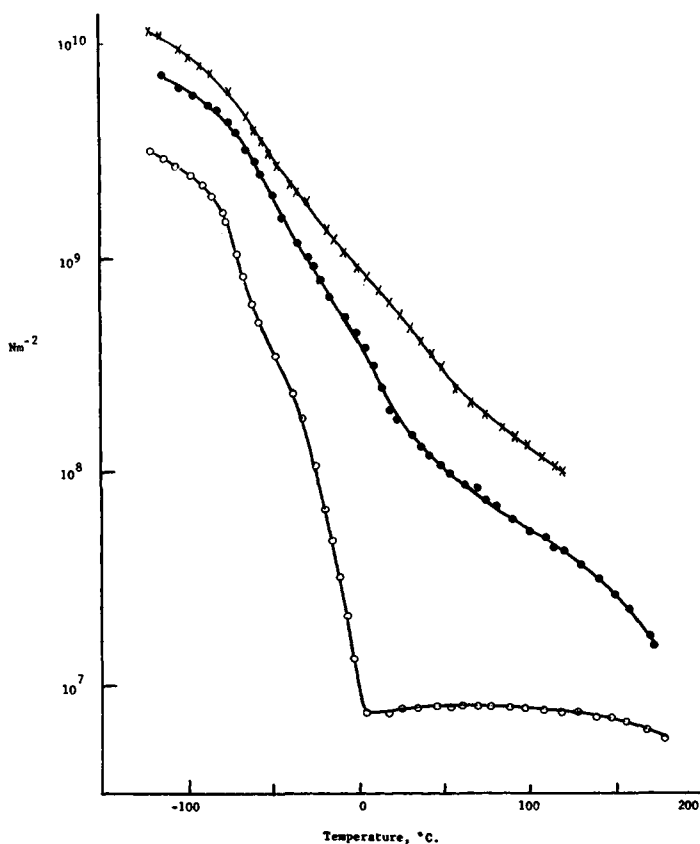


Fig. 5. Storage modulus (E') vs. temperature for Lycra at 110 Hz and 2% (○), 200% (●) and 400% (×) static strain.

Using values of 98°C ²⁰ and -85°C ²² for the glass transition temperatures of polyacrylonitrile and polybutadiene, respectively, eq. (1) predicts a value of -45°C , while eq. (2) gives a value of -36°C . However, a glass transition temperature of -46°C has been reported²² for polybutadiene, and this leads to a value of -10°C , which may be compared with -12°C for 2% static strain.

Lycra and Spanzelle

The relative ease with which polyurethane elastomers can be tailor-made makes them an ideal class of compound for the study of structure-property relations. Many changes in physical properties caused by composition variations have been reported by Saunders²⁴ and Saunders and Frisch.²⁵ It seems clear that the low-temperature mechanical behavior of urethane elastomers depends to a large extent on the nature of the polyester or polyether soft-segment structure,²⁶ whereas any high temperature transition finds its origins in the hard-segment region of the segmented polyurethane.

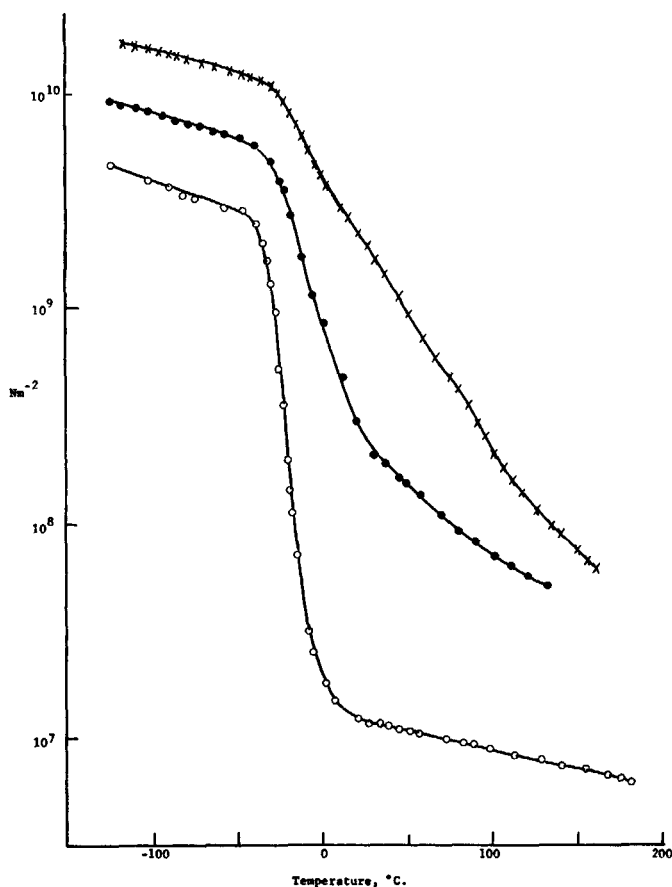


Fig. 6. Storage modulus (E') vs. temperature for Spanzelle at 110 Hz and 2% (O), 200% (●) and 400% (X) static strain.

These two threads both showed more than one transition, and these will be referred to as the α , β , and γ transitions in order of decreasing temperature.

Figures 5 and 6 show the dynamic storage modulus temperature relations for Lycra and Spanzelle, respectively.

Clough, Schneider, and King¹⁴ have stated that domain ordering occurs to a higher degree in polyether- than in polyester-based elastomers. The occurrence of a transition around 150°C agrees very well with the findings of Clough and Schneider⁸ who have reported a similar transition for various polyurethanes and have ascribed it to domain breakdown. They observed the transition for both polyester- and polyether-based polyurethanes, but the effect was more marked for the polyether-based soft-segment polyurethane. This was also clearly so in this work, although in both cases measurements could not be made much in excess of 150°C because of sample failure. In fact, Spanzelle at 200% strain and Lycra at 400% strain failed prior to this temperature.



Fig. 7. Loss modulus (E'') vs. temperature for Lycra at 110 Hz and 2% (O), 200% (●) and 400% (×) static strain.

Figures 7 and 8 show E'' versus temperature for Lycra and Spanzelle, respectively. Both elastomers show a γ transition at the low-temperature side of the glass transition. This occurs at a lower temperature for Lycra, which has polyether soft segments, than for Spanzelle, with polyester-based flexible units. Low-temperature relaxations have been found for a wide range of polymers which differ considerably in structure. Schatzki¹¹ has proposed that the γ relaxation is caused by hindered rotation of short methylene sequences which may be located either in the chain backbone or in side chains. The Schatzki model proposes that the terminal bonds of the rotating unit are colinear and fixed in space. To meet these conditions and still have a possible conformation, there must be at least six methylene units in the sequence. In the crystalline phase, the methylene

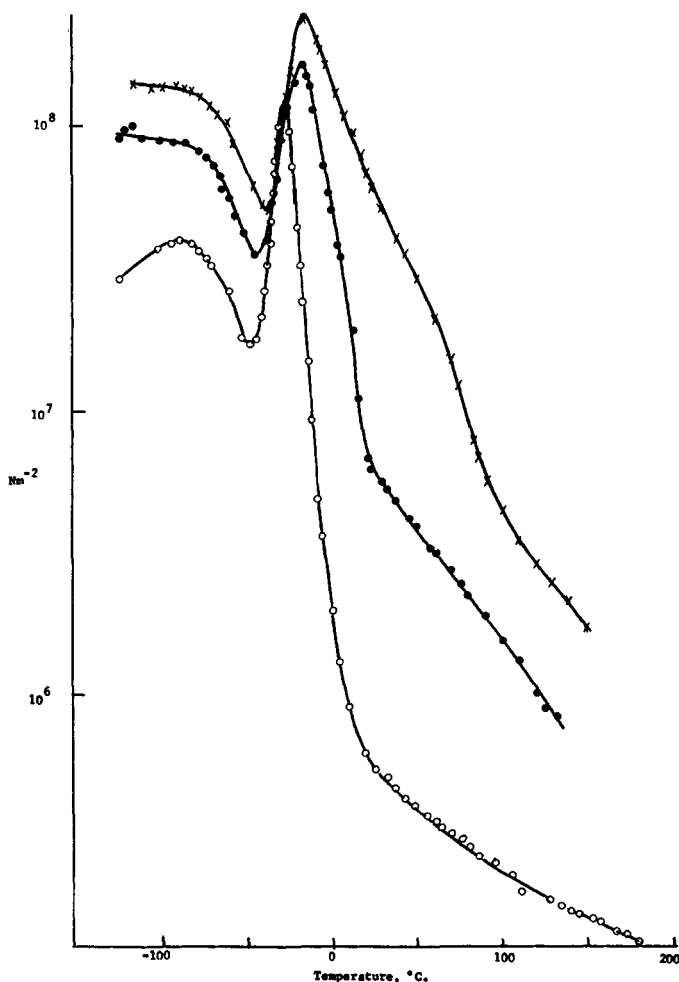


Fig. 8. Loss modulus (E'') vs. temperature for Spanzelle at 110 Hz and 2% (○), 200% (●) and 400% (×) static strain.

groups are in the trans conformation, and this does not permit colinearity of the terminal bonds as required by this mechanism. However, for polyethylene,²⁷ an ethylene-methacrylic acid copolymer,²⁸ and poly(chlorotrifluoroethylene),²⁹ it has been shown that the γ transition originates partly in the crystalline phase. Thus, it is possible that this could also be the case for polyurethanes. For Lycra, the γ peak in Figure 7 does not change much over the entire range of static strain, but this does not rule out a crystalline phase contribution as the decrease in the amorphous phase component of the γ peak could be being offset by an increase in the component from the crystalline phase.

Kajiyama and MacKnight⁹ have reported the "essential" absence of a γ peak in the two laboratory-prepared polyurethanes containing only two

or three methylene units in each soft segment when there was no methylene sequences in the hard segment. Only when more methylene units were introduced did a γ peak occur, thus clearly indicating the operation of a Schatzki-type mechanism. For Lycra, there are four methylene groups in each repeat unit in the soft segment. As the γ peak is well developed, it has to be assumed that if a Schatzki-type mechanism holds, then one or both of the ether oxygen atoms must also be involved in the rotation. At 2% static strain, the γ peak was at -130°C , but at 200% and 400%, it occurred 15°C lower. This may be due either to the breakdown of some hydrogen bonding at higher strains or to an increase in free volume. Both would result in an increased ease of rotation.

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