

# MECHANICAL BEHAVIORS OF POLYURETHANE-UREA ELASTOMERIC FIBERS UNDER STATIC STRETCHING DEFORMATION

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## ABSTRACT

The mechanical behaviors of polyether (ET) and polyester (ES) soft segment urethane-urea elastomeric fibers constrained at different levels of elongation have been investigated by means of dynamic mechanical tests and force-temperature measurements. The dynamic mechanical response of the ET urethane-urea showed some difference from that of the ES as a function of extension ratio. For force-temperature measuring the existence of a low temperature transition corresponding to the glass transition ( $T_g'$ ) of the ester or ether soft segments, stress-softening temperature ( $T_s$ ) and initial melting temperature ( $T_{mh}$ ) of hard segment crystallites was observed. The result of cyclic testing of a constrained sample as a function of temperature indicated that the irreversible decrease in stress implied a permanent change in sample microstructure.

## INTRODUCTION

Linear thermoplastic elastomers based on polyurethane block copolymers have been the object of considerable research interest in recent years due to their excellent physical characteristics. These materials are heterophase systems composed of alternating aromatic urethane with a low molecular weight chain extender as the hard segment and a low molecular weight rubbery polymer as the soft segment. Extensive studies<sup>[1-7]</sup> have concluded that the hard blocks of the polyurethane copolymer segregate and form domains or clusters because of the presence of crystallinity and/or inter- and intra-molecular hydrogen bonding in the isocyanate groups. These domains function as physical crosslinks and filler particles which reinforce the rubbery matrix<sup>[8-10]</sup>. Studies of transition phenomena including the glass transition and melting transition, and of morphological changes are important for both the design and application of this kind of elastomer.

It has been recognized that the excellent physical and mechanical characteristics of polyurethanes come from the incompatibility of the soft and hard blocks, resulting in microphase separation with the hard segment domains dispersed in a soft matrix. The deformation

behavior of an elastomer is not only dependent on its original composition and morphology, but also on the type and level of the deformation applied to the elastomer, which can promote changes of the microstructure and morphology of the material<sup>[11]</sup>. Dynamic mechanical studies to date have investigated the effects of changes in the composition ratio of hard and soft segments and the influence of thermal history on polyurethanes<sup>[4,12,13]</sup>. These studies have been successful in elucidating the molecular mechanisms underlying the mechanical behavior of these materials. One serious drawback of this method is that no hard segment relaxation can be detected due to the low modulus of these materials above the glass transition temperature of the soft segments. Also, the amount of polyurea hard segments in the samples tested is so low that it is very difficult to study the domain morphology change directly by means of light and/or electron microscopy, because of the diffuse boundary between the hard and soft domains. In this paper a comparison of dynamic mechanical (DM) and differential scanning calorimetry (DSC) results is presented which clarifies the role of uniaxial prestrain on the dynamic mechanical behavior of polyurethane-urea elastomers and force-temperature curves at various draw ratios may provide important information concerning soft and hard segment melting with temperature and extension, unobtainable by other methods.

## EXPERIMENTAL

The materials used were linear polyether and polyester based urethane-urea elastomeric fibers. The hard blocks of polyurethane-urea segments were made of 4,4'-diphenylmethane diisocyanate (MDI) with ethylene diamine as the chain extender. The amount of hard segment in the polyurethane-urea block copolymer was about 15% by weight. The soft blocks of the polyether urethane-urea were based on polytetramethylene-oxide (PTMO) having a prepolymer weight average molecular weight  $M_w=2000$ . Soft segments of the polyester urethane-urea were composed of a mixture of ethylene glycol, butanediol and adipic acid having a prepolymer  $M_w=3500$ .

### *Dynamic measurement*

All measurements were carried out using a Vibron dynamic viscoelastometer, PL Rheovibron (made in England), at a fixed frequency of 1 Hz over a temperature range of  $-130$  to  $120^\circ\text{C}$ . A constant heating rate of  $4^\circ\text{C}/\text{min}$  was used for all experiments.

In this equipment the dynamic strain is imposed in a bending mode, not the uniaxial stretching mode of similar instruments. Sample preparation involves dead weight loading of the sample to obtain the desired elongation. The final diameter and length of the fiber are measured and the elongated sample is wound onto the frame in a single close-packed layer and the ends are fixed to prevent contraction of the fibers during the dynamic testing.

### *Differential scanning calorimetry (DSC)*

Differential scanning calorimetry measurements were performed on constrained fibers of ET and ES urethane-urea using a Perkin Elmer DSC 2 differential scanning calorimeter. Scans were conducted from  $150$  to  $510^\circ\text{K}$  at  $10^\circ\text{C}/\text{min}$ . The preparation and DSC measurements of fiber samples held at constant strain have been published elsewhere<sup>[14]</sup>.

### *Force versus temperature measurements*

The measurements were carried out using the apparatus which consisted of a glass heating chamber, nitrogen gas system, load cell, stretching metal rod, thermocouple, amplifier and recorder. The sample was made into a loop with the ends knotted and hung between the hooks. One end was connected to the load cell and the other end to a rod which was used to change the draw ratio of the sample. A constant heating and cooling rate of  $5^{\circ}\text{C}/\text{min}$  over the temperature range  $-80$  to  $200^{\circ}\text{C}$ , was used for all experiments.

### *Measurement of residual strain*

Measurements of the residual strain of samples which were subjected to different temperatures and draw ratios were carried out as follows: for test temperatures above room temperature, the sample was stretched at room temperature and then put into an oven for heat treatment at the elevated temperature. The sample was then removed and held at room temperature for a few days before measuring the residual strain. For sub-ambient thermal treatment, the sample was first cooled to the desired temperature and then stretched, followed by the same procedure mentioned previously.

## RESULTS AND DISCUSSION

### *Results of dynamic mechanical measurements of unstrained samples*

For general dynamic behavior of ET and ES urethane-urea elastomeric fibers there are three loss peaks at about  $-105$ ,  $-42$  and  $21^{\circ}\text{C}$  ( $\gamma$ ,  $\alpha_a$  and  $\alpha_c$ ) for ET and three loss peaks at about  $-98$ ,  $-65$  and  $-22^{\circ}\text{C}$  ( $\gamma$ ,  $\beta$  and  $\alpha_a$ ) for ES. These results are similar to the dynamic results given by Huh and coworker<sup>[4]</sup>. Usually, the  $\gamma$  peak observed in segmented polyurethanes is assigned to a local motion of the methylene sequences in the prepolymer segments or of the diol portion in the hard segments. The  $\beta$  peak observed in ES urethanes is assigned to the motion of NH or C=O groups. The  $\alpha_a$  peak observed in all the polyurethane block polymers is assigned to the micro-Brownian motion of amorphous macroglycol segments. The  $\alpha_c$  peak observed in ET urethanes might be assigned to a melting process in the crystalline phase of the prepolymer segments and was not found in the ES urethane-urea used in this study. No hard-segment relaxation can be detected by dynamic mechanical testing because of the low modulus of these materials above the  $\alpha_a$  relaxation.

### *Results of dynamic mechanical measurements of elongated samples*

The dynamic mechanical behavior of ET and ES based urethane-urea elastomeric fibers constrained at different levels of elongation ( $\lambda = \frac{L}{L_0}$ ) is shown in Figures 1a and 1b. For ET urethane-urea the peak temperature of the  $\alpha_a$  transition shifts to higher temperatures with increasing draw ratios. The intensity of the peak decreases gradually and the top of the peak is broadened. This phenomenon suggests that the degree of crystallinity of the soft segments

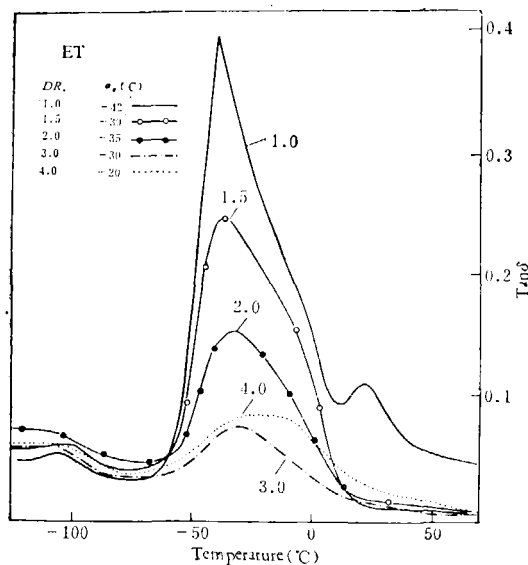


Fig. 1a Temperature dependence of loss tangent for ET polyurethane-urea at diff. draw ratios and 1 Hz

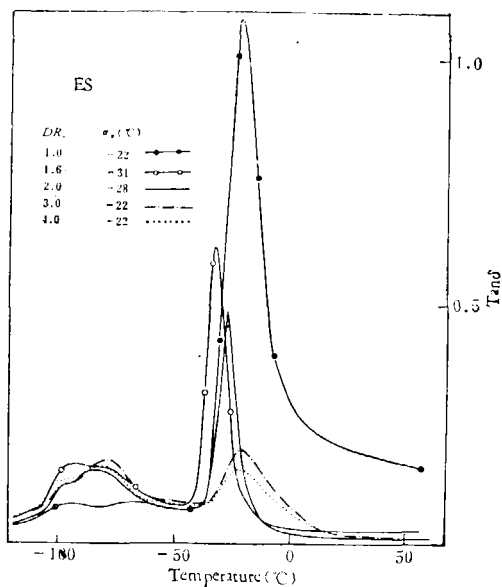


Fig. 1b Temperature dependence of loss tangent for ES polyurethane-urea at diff. draw ratios and 1 Hz

increases with increasing draw ratio due to strain-induced crystallization. The crystallites function in the soft segment domains as physical crosslinks which tend to restrict motion in the rubbery phase shifting the  $\alpha_a$  dispersion to a higher temperature. This result is consistent with the usual observations in semi-crystalline homopolymers, where increasing the crystalline fraction usually depresses the major relaxation of the remaining amorphous chains and shifts the  $T_{g's}$  to slightly higher temperature<sup>[15,16]</sup>. This observation is supported by DSC results on constrained samples at various elongations as shown in Figure 4a. The endothermal peaks corresponding to melting of the soft segments move to higher temperature, while the  $\alpha_c$  peak diminishes for small draw ratios. This process is shown in detail in Figure 2 where the intensity of the  $\alpha_c$  peak decreased very sharply with increasing draw ratio and disappeared or merged to a new strain-induced crystallization peak. These observations suggest that the  $\alpha_c$  relaxation could be due to a melting process of the small imperfect crystallites or a relaxation of interactions between the soft and hard segments which are broken by deformation. Results from dynamic mechanical measurements of the ET fiber and solution-cast films indicate the  $\alpha_c$  peak does not result from the fiber spinning process.

For the ES urethane-urea the major peak,  $\alpha_a$ , is a single peak and no  $\alpha_c$  peak can be seen in dynamic figure, indicating the soft blocks are amorphous. It is interesting to note that the  $\alpha_a$  peak tends to shift to lower temperatures for draw ratios  $\lambda < 2$ . For draw ratios greater than two the relaxation temperature of the  $\alpha_a$  peak moves back to higher temperatures while the intensity decreases gradually. The change of the  $\alpha_a$  peak for draw ratios between 1.0 and 3.0 are shown in Figures 3a and 3b. These results are consistent with DSC data where no endothermal peak corresponding to a melting point of the soft segments was observed below

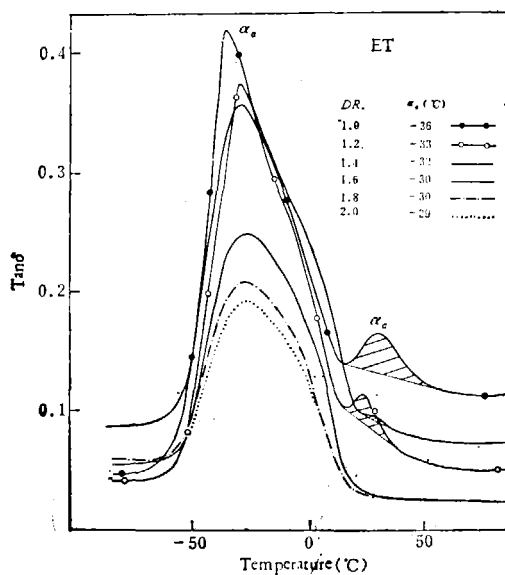


Fig. 2 Temperature dependence of loss tangent for ET polyurethane-urea within small draw ratios at 1 Hz

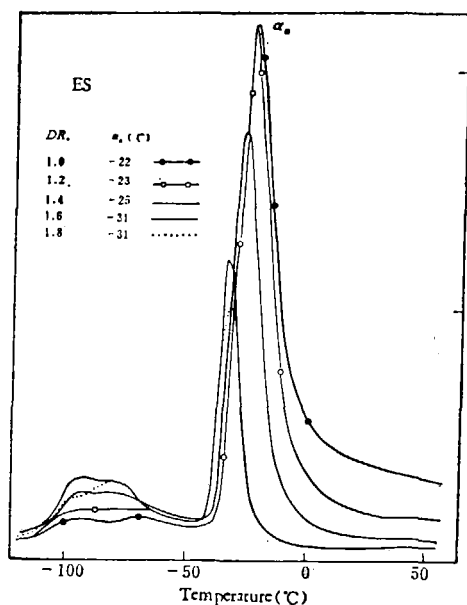


Fig. 3a Temperature dependence of loss tangent for ES polyurethane-urea within small draw ratios at 1 Hz

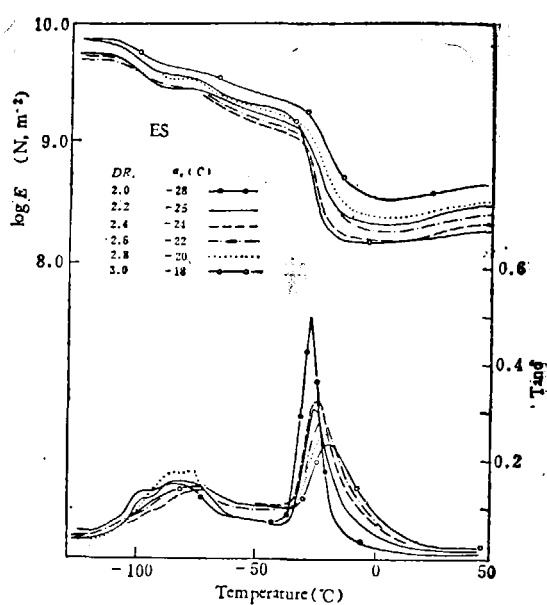


Fig. 3b Temperature dependence of loss tangent for ES polyurethane-urea within small draw ratios at 1 Hz

$\lambda < 2.0$ . However, once crystallization occurs, the endotherm moves gradually to higher temperature as shown in Figure 4b. The combined results of the dynamic mechanical and DSC measurements indicate a strong interaction between strain-induced crystallization and mechanical properties in the ES based polyurethane-urea. For  $\lambda < 2.0$  it is possible that the decrease in  $T_g$ , results from the phase separation between the soft and hard segments, e.g., the small amounts of hard segments mixed in the soft segments are transferred to the hard segment phase during the stretching process resulting in a relatively pure soft segment phase. At high draw ratios, strain-induced crystallization can occur in the soft segment phase. The change of the soft segment glass transition temperature with extension, obtained from dynamic mechanical measurements, is shown in Figure 5 for both types of polyurethane-urea elastomers.

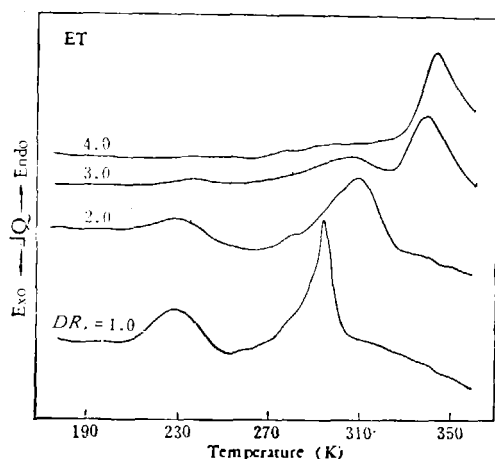


Fig. 4a DSC results for ET polyurethane-urea at diff. draw ratios

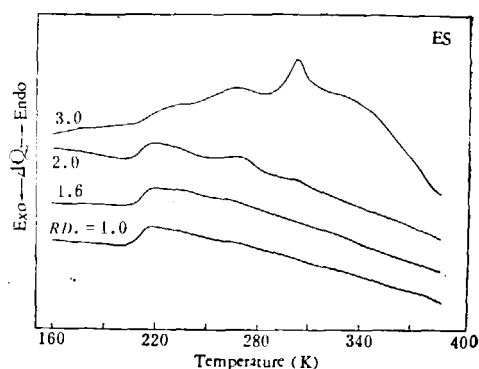


Fig. 4b DSC results for ES polyurethane-urea at diff. draw ratios

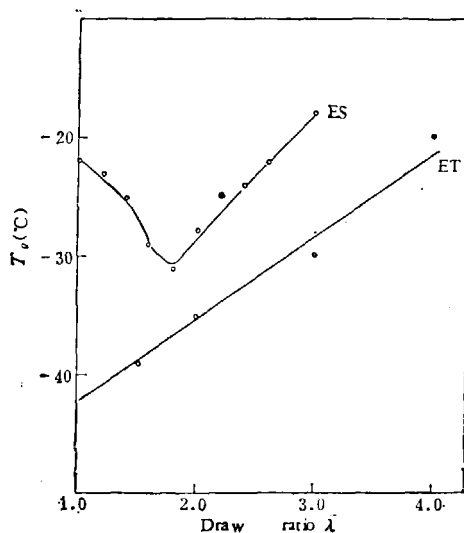


Fig. 5 The relationship between  $T_g'$  and draw ratio for both ET and ES polyurethane-urea

### Results of force-temperature measurements of elongated samples

The force-temperature behavior of both ES and ET soft segment fibers as function of draw ratio is shown in Figures 6a and 6b. The dotted line in each figure shows the cooling curve, and the solid line shows the heating curve. Three thermal transitions are observed, corresponding to the glass transition of the soft segments ( $T_{g's}$ ), the stress-softening temperature ( $T_s$ ), and the initial melting temperature of the hard segments ( $T_{mh}$ ). As shown in these figures, below the soft segment glass transition these polyurethane-ureas exhibit typical positive thermal expansion. Above  $T_{g's}$ , however, the soft segments can move freely, and the stress increases with increasing temperature due to the negative thermal expansion coefficient of the extended rubbery phase. It is noted that the temperatures of the three thermal transitions on the force-temperature curves change with draw ratio. The strain dependence of the three transition temperatures for both ES and ET soft segment fibers are summarized in Figures 7a and 7b. The change in  $T_{g's}$  is supported by DMTA and DSC results on constrained samples at various elongation as mentioned above. The influence of strain-induced crystallization on the force-temperature curves is also observed. For draw ratios greater than three, there is a hysteresis between the heating and cooling curves which increases with increasing draw ratio. This indicates crystallization of the soft segments during the cooling process. This phenomenon is similar to that of natural rubber<sup>[17]</sup> in which an uniaxial deformation induces a crystallization

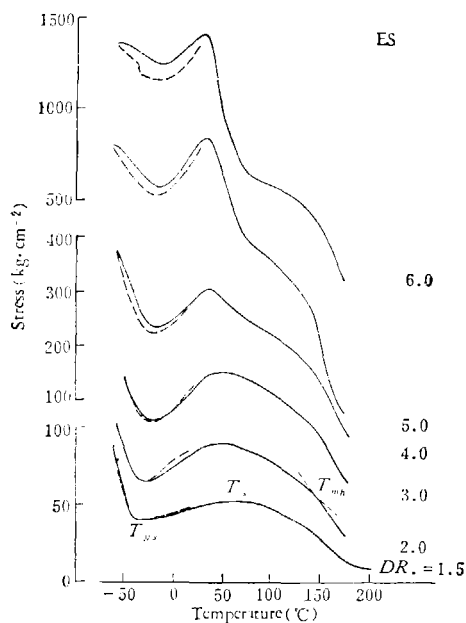


Fig. 6a Force versus temperature curves for ES polyurethane-urea at diff. draw ratios

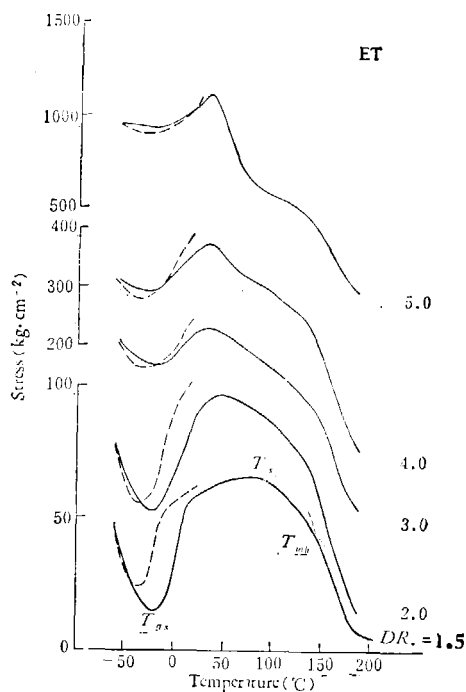


Fig. 6b Force versus temperature curves for ET polyurethane-urea at diff. draw ratios

process that occurs in two stages. The first stage is strain dependent and is characterized by a molecular orientation along the strain direction. The second stage occurs under suitable thermodynamic conditions, in particular, on cooling of the stretched sample, and is characterized by growth on the primary structure.

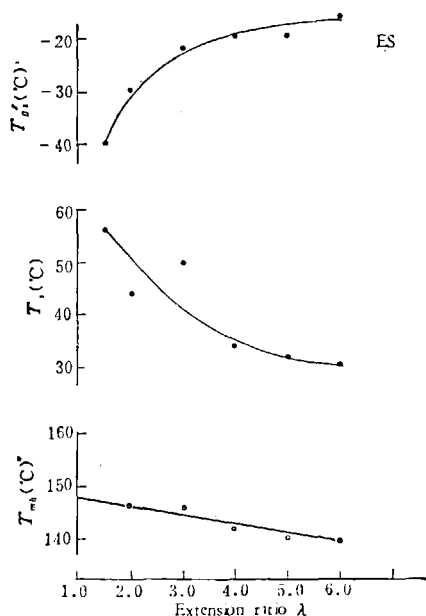


Fig. 7a Strain dependence of  $T_{g's}$ ,  $T_s$  and  $T_{mh}$  for ES polyurethane-urea

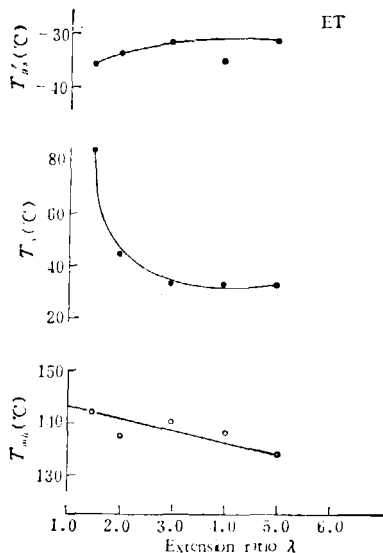


Fig. 7b Strain dependence of  $T_{g's}$ ,  $T_s$  and  $T_{mh}$  for ET polyurethane-urea

The results of DSC under uniaxial deformation indicate the melting point of the soft segments increases with increasing draw ratio for both of these polyurethane-urea elastomers. Conversely, the stress softening temperature on the force-temperature curves is shifted to lower temperature with increasing draw ratio. Consequently, stress-softening of these materials may imply some changes in the microstructure, which controls rigidity of the material. It is now widely accepted that polyurethanes are heterophase polymers. The hard segment domains dispersed in the rubbery matrix reinforce the material by functioning both as physical crosslinks and filler particles. This is believed to be responsible for the high tensile strength and modulus. However, the presence of domains may also be responsible for the thermal stress-softening of the materials. Similar to chemically elastomers in which the stress relaxation is related to bond breaking, the thermal softening of linear polyurethane-ureas could be related to changes of the hard domains, such as orientation or slippage caused by deformation. It is known that the typical polyurethane is extensively hydrogen bonding and hydrogen bonding between hard and soft segments.

Infrared dichroism is a powerful and sensitive technique for investigating the morphology and deformation behavior of segmented polyurethanes. This is because one can assign a

specific IR band to the hard segment domain, soft segment phase and the interface between them, assuming that phase segregation is extensive. The change of the orientation function of both the hard and soft segments with deformation and temperature has been reported by Cooper and coworkers<sup>[18,19]</sup> using this technique. They found the orientation functions of both hard and soft segments increased with increasing draw ratio, but that the residual orientation of the hard segments was much larger than that of the soft segments. They also found a temperature dependence of the orientation function at a given strain level, where the orientation function increased gradually with increasing temperature up to a maximum, and then decreased rapidly. The sudden change of the orientation function with temperature was attributed to the onset of hydrogen bond dissociation occurring at the hard segment  $T_g$ . As for the sample used in this study, the amount of polyurea hard segment is small and exists in the sample as crystallites having a melting point for both ES and ET polyurethane-ureas occurs at around 210°C. The melting point of the hard segments is close to the decomposition temperature for both samples.

The sudden change of the orientation function with temperature may be related to the disruption of the interfacial hydrogen bonding between the hard and soft segment domains. This results in rearrangement and slippage of the domain structure which may be related to the residual strain of the sample. In order to explain the thermal stress-softening of these materials, a model for the change in the morphology of polyurethanes with deformation, developed by Bonart<sup>[20]</sup>, is shown in Figure 8. According to this model when a uniaxial strain is applied to a polyurethane elastomer the soft segments are immediately oriented in the stretching direction, causing a shearing stress which then disrupts the structure and orients the hard domains in the stretching direction. There may also be considerable soft segment crystallization with stretch. This process may be influenced by temperature.

Figure 9 shows a cyclic force versus temperature experiment in which the ES urethane-urea is cycled to a higher maximum temperature with each successive cycle. It is seen that the force-temperature response is highly dependent on the maximum temperature of the cycle,

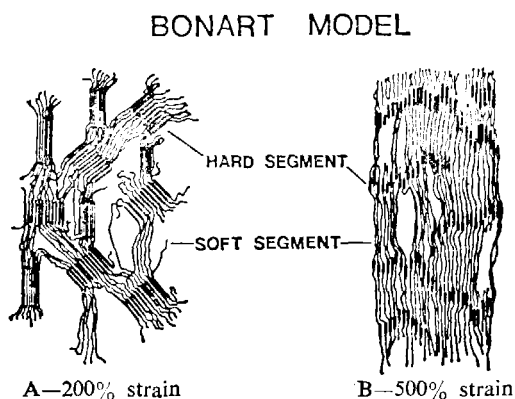


Fig. 8 Bonart model for the change in the morphology of polyurethane with deformation

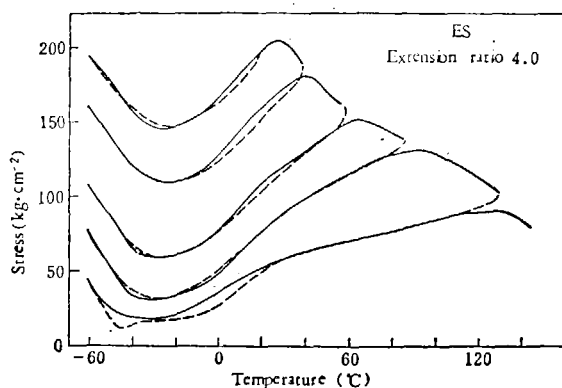


Fig. 9 Temperature dependence of retractive stress for ES polyurethane-urea of cyclic testing at  $DR=4.0$

as evidenced by a decrease of the stress and a subsequent increase in the residual strain of the sample. The temperature dependence of the residual strain for both ES and ET soft segment fibers as a function of draw ratio is shown in Figures 10a and 10b. Indeed, there is an inflection on each curve. The plot of this turning point temperature versus draw ratio exhibits the same trend as the results of the deformation dependence of  $T_i$  as shown in Figure 11. Both sets of experimental results are not in good agreement, however. For large deformations the residual strain shows less temperature sensitivity than the softening temperature of the force-temperature data. This difference may be due to the fact that strain-induced crystallization of the soft segments is present at higher extensions. For draw ratios  $\lambda \leq 2$ , no appreciable strain-induced crystallization of the soft segments occurs. With increasing draw ratio, however, the contribution of strain-induced crystallization of soft segments to the retractive force may be significant. Since there are two peaks for strain-induced crystallization on the DSC curves mentioned above, the one which appears at lower temperature may be responsible for the thermal softening at lower temperature for large deformation.

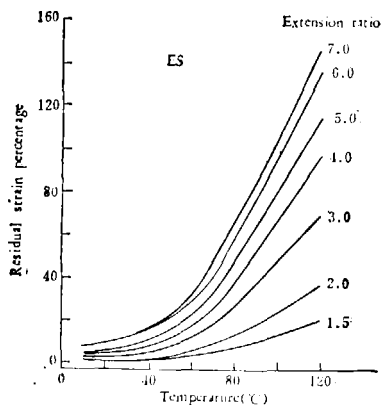


Fig. 10a Temperature dependence of residual strain percentage for ES polyurethane-urea at diff. draw ratios

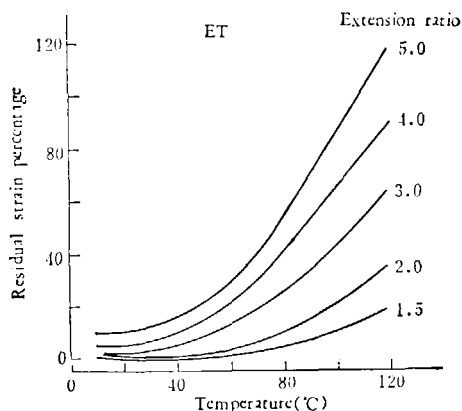


Fig. 10b Temperature dependence of residual strain percentage for ET polyurethane-urea at diff. draw ratios

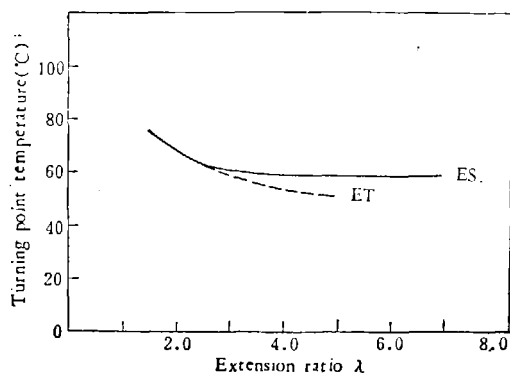


Fig. 11 Relationship between the turning point temperature and draw ratio for both ET and ES polyurethane-urea

As mentioned previously,  $T_{mh}$  is the initial melting point of the polyurea hard segments. For small draw ratios the applied stress causes such a small shearing force that it is difficult to determine  $T_{mh}$  from an inflection in the force-temperature curve. With increasing draw ratio, the position of  $T_{mh}$  becomes clearer. Extrapolating the curve of  $T_{mh}$  versus draw ratio to zero strain ( $\lambda=1$ ), a  $T_{mh}$  of the unstrained sample is found to be about 150°C and both polyurethane-ureas show similar results.

## CONCLUSIONS

Dynamic mechanical measurements on strained samples of polyether and polyester soft segment polyurethane-ureas demonstrate a shifting of the glass transition temperature of the soft segments with strain. This observation correlates with DSC experiments on stretching samples showing shifts in the  $T_m$  of the soft segments. This phenomena is complicated by strain-induced crystallization and probable mixing or separation of the two phases with strain. The unstrained ET urethane-urea shows some crystallinity in the soft segments which increases with strain, causing  $T_g$  and  $T_m$  to shift to higher temperatures. The ES urethane-urea shows the predominant feature of lowering the temperature of the soft segment glass transition for small stretch ratios and then increasing the  $T_g$ , for large stretch ratios. This has been interpreted as being due to phase separation of some mixed phases at small strains followed by strain-induced crystallization effects similar to those in the ET urethane-urea.

Investigations of the force-temperature behavior of same strained samples demonstrate the strain dependence of three thermal transitions corresponding to the glass transition of the soft segments ( $T_{g's}$ ), a stress-softening temperature ( $T_s$ ) and the initial melting point of the hard segments ( $T_{mh}$ ). The increase of  $T_{g's}$  with draw ratio is due to the orientation and strain-induced crystallization of the soft segments. Based on the reported irreversibility of the hard segment orientation function and the observed residual strain of the sample, the stress-softening phenomenon may be attributed to the orientation and rearrangement of the hard domains under extension. For large deformation the contribution of strain-induced crystallization to the retractive force may be a factor, which may explain the difference between force-temperature and residual strain data.

**Acknowledgement** The authors gratefully acknowledge the support for this research given by E. I. DuPont de Nemours & Company.

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