

MULTIPLE MELTING TRANSITIONS IN POLYURETHANE-UREA ELASTOMERS UNDER EXTENSION

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ABSTRACT

Two melting transitions were observed in linear segmented polyurethane-urea elastomers under extension using thermal, mechanical and X-ray diffraction techniques, and the results are compared. These data indicate both strain-induced and temperature-induced crystallization in the stretched elastomers, which may result from two different types of crystallites with different melting temperatures. These have been assigned as type 1 appearing around 60°C, and type 2 around 30°C. The type 1 crystallization can be induced by stretching at room temperature to large strain, and is mechanically reversible, but the type 2 crystallization is mainly induced by cooling below its crystallization temperature. These two crystalline structures are interchangeable under suitable conditions. At elongations greater than 300%, the low temperature peak observed on fusion thermograms disappears or combines with the high temperature peak. When the temperature of the sample is over the melting point of the type 1 crystal, irreversible melting occurs and only the type 2 crystal develops on cooling. The results of stress-strain and stress hysteresis experiments at different temperatures indicate the relative importance of strain-induced and temperature-induced crystallization on the mechanical properties of these materials.

INTRODUCTION

Polyurethane block copolymers are thermoplastic elastomers having unique properties which have been the subject of extensive study in recent years. These materials are formed by joining blocks of two chemically dissimilar segments along the polymer backbone. Typically these are hard (glassy or crystalline) and soft (rubbery or waxy) segments having glass transition temperature above and below the service temperature of the sample, respectively. The superior elastomeric properties can be attributed to physical crosslinking resulting from domain formation. The hard blocks are held together by intermolecular secondary bonding to form domains and serve as physical crosslinks for the rubbery matrix, while the soft blocks usually provide the polymer with extensibility.

Phase separation of the hard segments in urethane elastomers into microregions, termed domains, has been proposed based on the results of electron microscopy^[1], X-ray diffraction^[2,3]

and viscoelastic property measurements^[4,5]. The degree of microphase separation is strongly dependent on sample composition, segment molecular weight, morphology, capability of crystallization of either segment at experimental conditions and thermal history of the sample. Recently, the study of strain-induced crystallization and its influence on the deformation behavior of polyurethane elastomers has also been a subject of considerable interest.

In our previous papers, the strain-induced crystallization (SIC) of polyether and polyester soft segment elastomers has been reported. The SIC causes the glass transition (T_g) and melting temperature (T_m) of the soft segments to shift to higher temperature with strain. With increasing draw ratio the multiple melting transitions observed on fusion thermograms are attributed solely to the soft segments, since the amount of hard segment in these elastomers is very small and takes form of crystal with a melting point about 210°C.

It is well known that a stretched rubber network can crystallize when a suitable chain microstructure is present. Crystallization of a stretched polymer network may be initiated by two different mechanisms; SIC and temperature-induced crystallization (TIC). For example, Gehman and Field^[6,7,8] extensively studied the wide-angle X-ray scattering from natural rubber, and clearly demonstrated a dependency of crystal orientation and crystallinity on both elongation and subsequent cooling temperature. Yeh^[9,10] reported a transformation between two types of crystals with strain and temperature by means of electron microscopy and X-ray techniques. Hill and Keller^[11] published a similar investigation for crosslinked rubber-like polyethylene using wide angle X-ray diffraction. Their studies indicate two different types of crystals corresponding to a shish-kebab structure, supposedly consisting of extended-chain shish and folded-chain kebabs, in polyethylene crystallized under strain. The materials used in this study are considered to be crosslinked elastomers since the hard domains act as physical crosslinks in the rubbery matrix. The double melting peaks reported in the present work have also been shown in our previous paper. In the present study, however, the strain and temperature dependence of these will be described in more detail for polyether and polyester soft segment elastomers.

EXPERIMENTAL

Samples

The materials were linear polyether (ET) and polyester (ES) based polyurethane-urea elastomers composed of approximately 15% by weight hard segment and 85% by weight soft segment. The chemistry, properties and manufacture of these materials has been described^[12,13]. The hard blocks of polyurea segments were made of 4,4'-diphenylmethane diisocyanate (MDI) with ethylene-diamine as the chain extender. The soft blocks of the polyether were polytetramethylene-oxide (PTMO), having a prepolymer weight average molecular weight $\bar{M}_w=2000$. The soft blocks of the copolyester were synthesized from a mixture of ethylene glycol, butanediol and adipic acid and have a prepolymer $\bar{M}_w=3500$.

For differential scanning calorimetry (DSC), stress-strain and hysteresis measurements the samples used were commercially available coalesced multifilament yarns. The ET based

urethane-urea had a fiber denier of 1120 with a breaking strain of 500%, while the ES fiber denier was 650 with a 600% breaking strain. Films for wide-angle X-ray diffraction (WAXD) measurements were cast from a 3% by weight solution of the polymer in a 70/30 DMF/THF mixed solvent at a temperature of 60°C. All films were extensively dried at this temperature and then placed in a desiccator prior to investigation.

Apparatus and procedures

Thermal, X-ray and mechanical techniques were employed. Differential scanning calorimetry measurements were carried out using a Perkin-Elmer DSC-2, purged with helium and cooled with liquid nitrogen. Runs were performed on constrained fiber samples of about 40 mg at a heating rate of 10°C/min. The preparation and DSC measurement of fiber samples held at constant strain has been published previously^[14].

Wide angle X-ray diffraction scans were obtained on 1.0 mm thick solution-cast films using a Siemens D500 diffractometer employing a nickel filtered $\text{CuK}\alpha$ radiation generator operated at 45 kV and 27 mA. Data were collected between 4° and $35^\circ 2\theta$, at a scan rate of $1^\circ/\text{min}$. Intensity, recorded as a counting rate, was plotted versus angle on a strip chart recorder. In order to record X-ray scattering from stretched specimens at different temperatures, a combination stretcher-temperature device was designed to fit the instrument. The basic frame has two clamps to maintain the specimen in a strained condition, both of which can move independently. Nitrogen gas, maintained at $\pm 1^\circ\text{C}$ of the desired temperature, was circulated around the sample. Temperature measurements were made near the point where the X-ray beam passed through the sample.

Stress-strain measurements were performed on fibers using an Instron Hydraulic Tensile Tester fitted with a specially designed environmental chamber with high and low temperature capability.

RESULTS AND DISCUSSION

Differential scanning calorimetry data are given in Figures 1 and 2 for ET and ES based urethane-urea elastomers, respectively, showing the occurrence of strain-induced crystallization. A comparison of the melting characteristics shows that the unstrained ET sample displays some quiescent crystallinity of the polyether soft segments but that the polyester soft segments of the ES material are amorphous. Early studies on similar materials using infrared spectroscopy have demonstrated that N—H groups are predominantly bonded to urethane C=O in ET urethanes, and to urethane and ester C=O groups in ES urethanes. Since N—H bonding to the ether is weaker than to the urethane C=O there is more extensive phase separation in polyether based urethanes than in those with polyester soft segments. This is in agreement with the results of dynamic mechanical testing on similar materials reported in our previous paper. In these studies the major relaxation of polyester soft segments decreased with strain up to an extension ratio $\left(\lambda = \frac{L}{L_0}\right)$ of 1.8, and then increased with increasing extension ratio due to orientation and strain-induced crystallization of the soft segments. Differential scanning

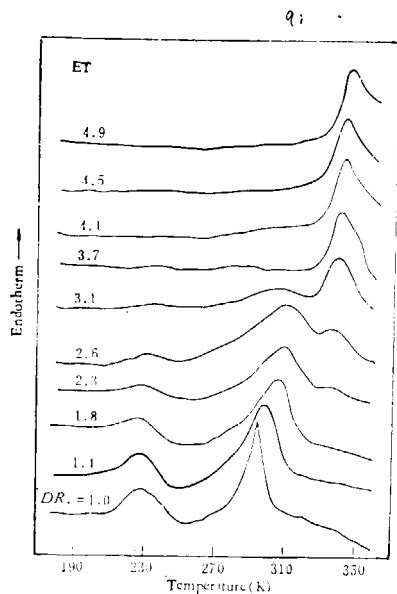


Fig. 1 DSC diagrams of ET polyurethane-urea at diff. draw ratios

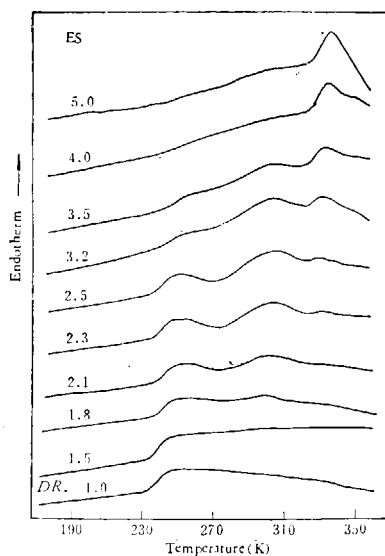


Fig. 2 DSC diagrams of ES polyurethane-urea at diff. draw ratios

calorimetry results for both ET and ES urethane-ureas exhibited two melting transitions at $\lambda \geq 2.3$. With increasing extension ratio the higher melting endotherms increased sharply, while the low temperature peak was reduced and eventually disappeared at $\lambda = 4.0$. The existence of two melting peaks may be attributed to different types of crystallites present in these elastomers when crystallization occurs under strain; type 1 with a higher melting point strongly depends on strain, while type 2 appears mainly after cooling. This is supported by WAXD data on both ET and ES samples under strain as shown in Figures 3 and 4.

No hard segment crystalline reflections sign can be observed on these scans due to the low amount of hard segment in the samples. However, the data do show a large increase in diffraction intensity at $\lambda = 3.0$. Comparison with differential scanning calorimetry data indicates that the diffraction peak arises mainly from type 1 crystallites since the samples were stretched, and WAXD experiments performed, at room temperature. This was close to or above the melting temperature of type 2 crystallites. Both figures show that the intensity of the diffraction peak increases with increasing draw ratio.

Figures 5 and 6 show some DSC data which suggests the non-equilibrium nature of type 1 crystallites. As shown in Figure 5, after heating a constrained sample at 90°C for one hour, which is over the melting point of type 1 crystallites, the associated endotherm disappears and only type 2 crystallites persist on A' and C' curves. If the sample which was relaxed after annealing is restricted, the double melting transitions reappear on the fusion thermograms, and the melting point of the type 2 crystallites is unchanged. Since the high temperature endotherm represents crystallization which has occurred due to orientation of the chain axes in the stretch direction, the amount of this type of crystallinity should increase with strain and exhibit strain reversibility. When the temperature exceeds this melting point, increased mobility

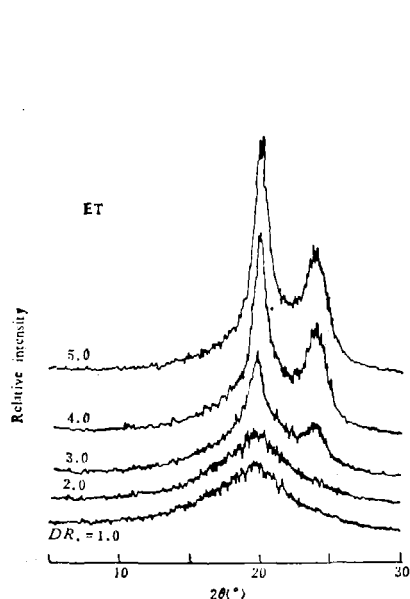


Fig. 3 WAXD curves for ET polyurethane-urea at diff. draw ratios

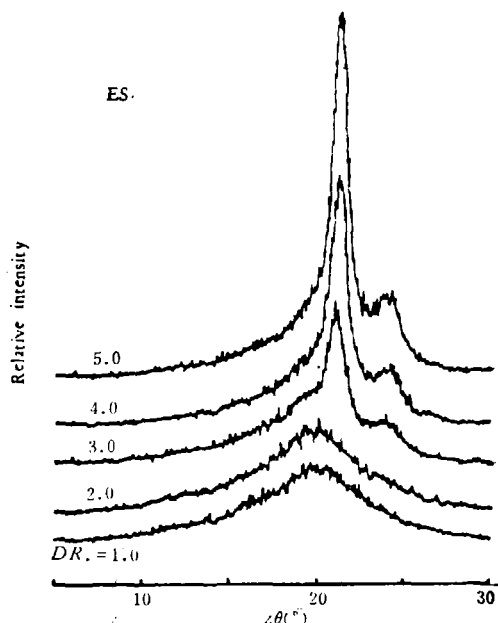


Fig. 4 WAXD curves for ES polyurethane-urea at diff. draw ratios

allows for a reorganization of stresses accompanying disorientation of chain axes the extended-chain crystal ties melt irreversibly at fixed extension and type 2 crystals develop during cooling. Type 2 crystals exhibit thermally reversible melting, and could be attributed to equilibrium folded-chain crystallites with less orientation dependence.

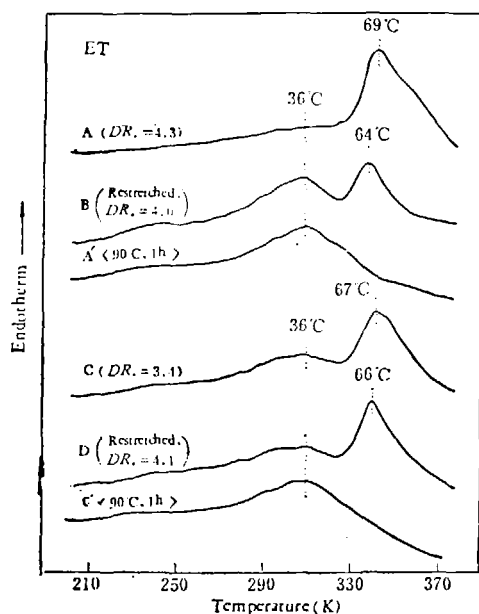


Fig. 5 DSC traces of ET polyurethane-urea at diff. treatment conditions

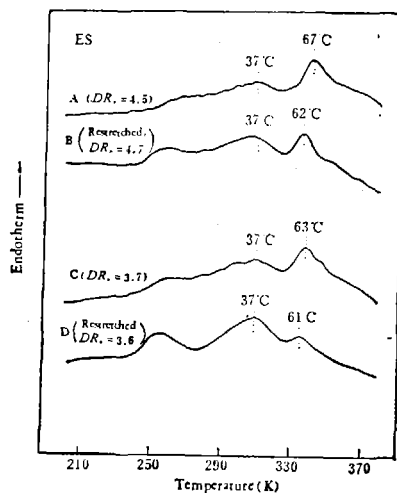


Fig. 6 DSC traces of ES polyurethane-urea at diff. treatment conditions

The reforming of strain-induced crystallites after annealing of constrained samples exhibits time dependence. This process is shown in detail in Figure 7. The sample of ES based urethane-urea was stretched to 300% strain at room temperature. Curve A shows a very sharp diffraction peak resulting from both types of crystallites. After annealing the constrained sample at 85°C for one hour, curve B reveals the absence of crystalline reflections similar to that of the unstretched sample. If the sample is relaxed at 85°C, and immediately restretched after cooling to room temperature, the diffraction peak reappears as shown in curve C. The intensity of this diffraction peak increases with increasing time in the relaxed state.

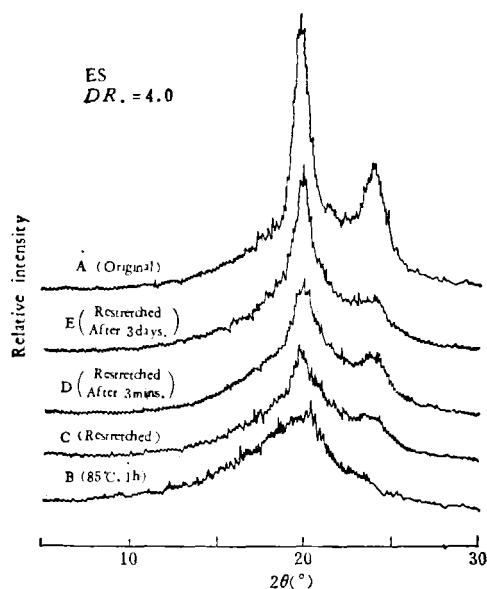


Fig. 7 WAXD curves for ES polyurethane-urea at diff. restretching conditions

As is well known, the excellent physical characteristics of polyurethane elastomers is attributed to the microphase structure of these materials. The hard segment domains, held together by intermolecular secondary bonding, function as physical crosslinks reinforcing the rubbery matrix. High levels of elongation provide not only strain-induced crystallization of the soft segment phase, but may also cause changes in the hard domains. During annealing of a constrained sample the homogenization of stress may occur with the orientation or slippage of hard domains. Return to an equilibrium distribution of these physical crosslinks depends on both temperature and time in the relaxed state. This could be one reason for the time dependence observed in the reforming of oriented crystallization.

The influence of strain and temperature on thermally-induced crystallization of ET based urethane-urea samples is shown in Figure 8. For unstretched samples the curves show little difference. This implies that the contribution of TIC to the intensity of the diffraction peak is negligible. Although an endotherm was observed on the DSC curve of the unstrained sample, this probably resulted from a folded-chain structure. With increasing draw ratio, TIC

becomes more evident. At constant strain, the amount of crystallinity in the oriented soft segments was increased significantly by a decrease in temperature. The change of the relative

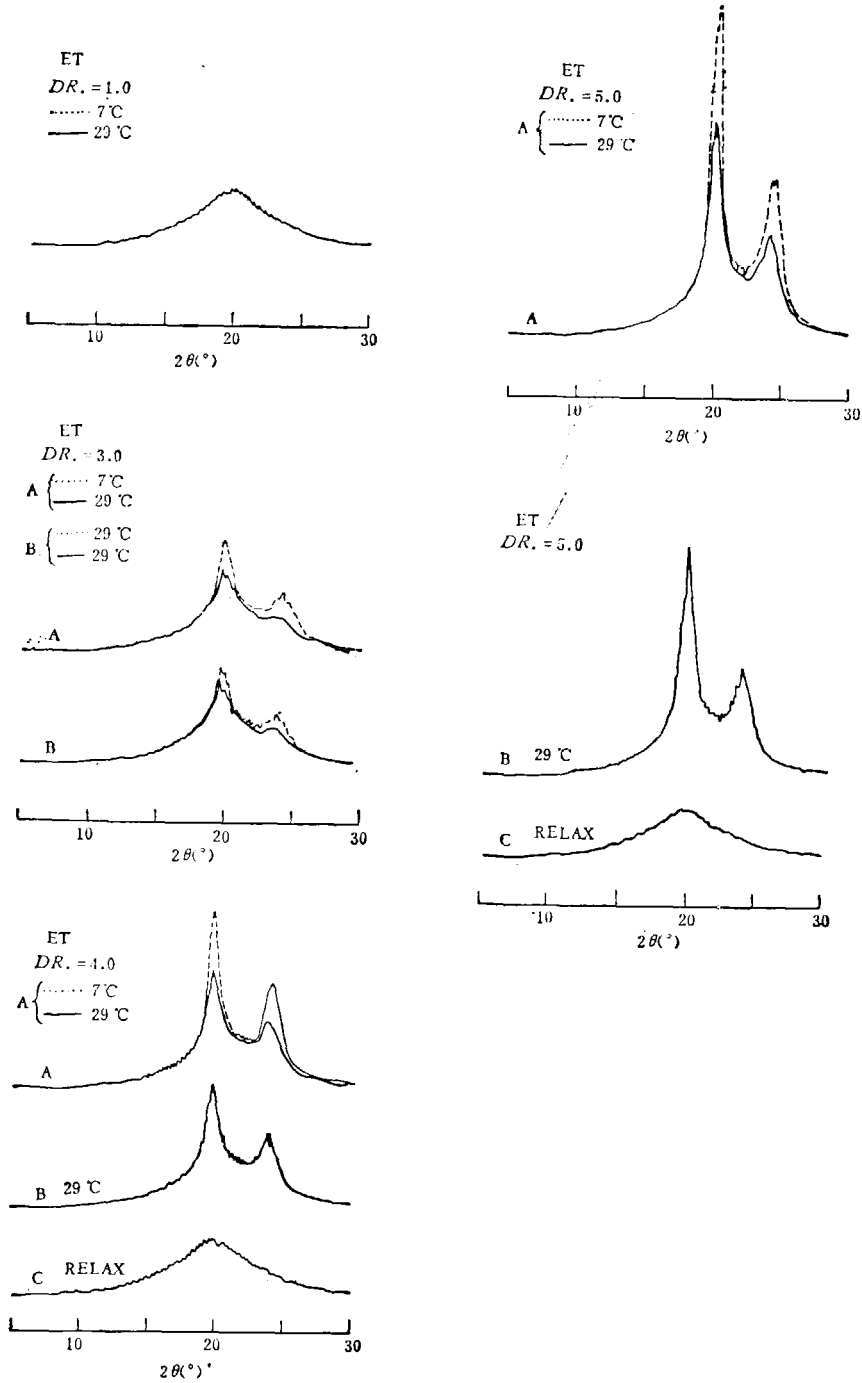


Fig. 8 WAXD curves of TIC for ET polyurethane-urea at diff. draw ratios

intensity of the diffraction peak on cooling indicates that TIC has a strong strain dependence. In particular, it is observed that the amount of TIC increases in proportion to strain. This may be due to the nucleation of thermally-induced crystallization on an existing strain-induced crystalline structure. The observed irreversible melting of TIC above $\lambda=3.0$, where SIC is fully developed and also melts irreversibly, suggests this interdependence.

The influence of strain-induced crystallization on the tensile properties of both ET and ES based urethane-urea elastomers is shown in Figures 9 and 10. In both figures, the slope of the stress-strain curve changes with strain and a large increase in stress is observed at $\lambda \geq 3.0$. This may be explained in terms of SIC of the soft segments as suggested by the DSC and WAXD data. The self-reinforcement of certain elastomers by the development of crystallinity on stretching is considered to be one of the mechanisms contributing to the strength of the elastomers. At temperatures over the melting point of the strain-induced crystals no stress enhancement is observed, as in the stress-strain curves performed above 60°C . Stress softening

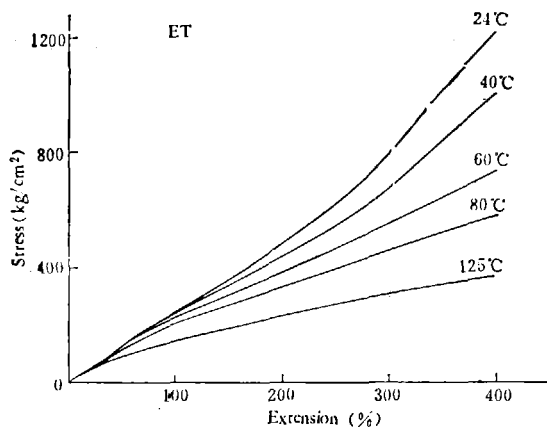


Fig. 9 Stress-strain curves for ET polyurethane-urea at diff. temperatures

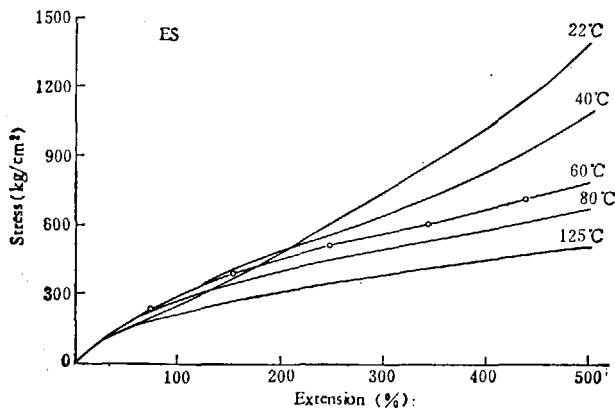


Fig. 10 Stress-strain curves for ES polyurethane-urea at diff. temperatures

may also result from rearrangement of hard domains which can lead to permanent deformation. This fact has been reported by several authors^[15-19].

The SIC also has a marked influence on the mechanical hysteresis under periodic deformation. Figures 11 and 12 show the relative hysteresis loss (K) as a function of temperature for both elastomers. Stress hysteresis measurements were carried out by loading and unloading the sample to increasing strain levels. The relative hysteresis loss ($K=A''/A'$) for a given cycle is calculated from the ratio of the area bounded by the loading-unloading curve (A'') to the area under the unloading curve (A'). These experimental results provide phenomenological data on the influence of the two different types of crystal on mechanical behavior. In a multiphase system, the stress hysteresis behavior is closely related to the domain morphology and phase composition^[20-22]. For polyurethane elastomers a possible mechanism of stress hysteresis can be attributed to ordered paracrystalline rearrangement of the hard and soft domains under periodic deformation. As seen in Figures 11 and 12, the relative hysteresis loss at room temperature increases rapidly with increasing extension ratio. With increasing temperature the dependence of the hysteresis loss on strain decreases. Especially above 60°C which corresponds to the melting temperature of strain-induced crystallization. This has been observed in several studies connecting SIC to the hysteresis behavior of elastomers^[23-25]. In view of this and previous data on the factors determining the relative contribution of thermal- and strain-induced crystallinity, it is clear that the latter are of primary importance in determining the mechanical behavior of polyurethane-urea elastomers.

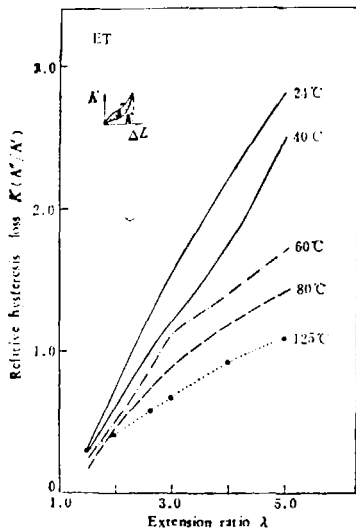


Fig. 11 Dependence of relative hysteresis loss on draw ratio for ET polyurethane-urea at diff. temperatures

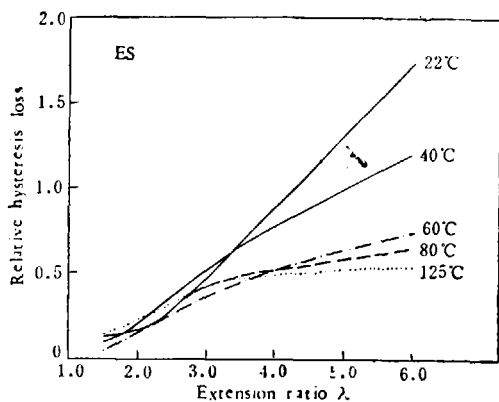


Fig. 12 Dependence of relative hysteresis loss on draw ratio for ES polyurethane-urea at diff. temperatures

CONCLUSIONS

The two melting transitions on fusion thermograms and interconversion of these under

suitable conditions has been studied for both ET and ES based urethane-urea elastomers under uniaxial deformation by means of different experimental techniques. The existence of two melting transitions is attributed to two different types of crystallite having different melting temperatures. Both exhibit strong strain and temperature dependence. The type 1 crystallites show strain reversibility while type 2 are thermally reversible.

The amount of strain-induced crystallinity increases most rapidly at an extension ratio of about three, increases almost linearly with strain and shows very little irreversibility. Mechanical experiments provide corroborative data concerning the existence of two different types of crystallites and their influence on mechanical behavior. Based on an analysis of the experimental results and comparison with data on natural rubber and elastic polyethylene under uniaxial deformation, it is suggested that the two different types of crystal may correspond to extended-chain and folded-chain structures. Direct evidence may be provided by electron microscopy, low-angle X-ray diffraction and low-angle light scattering.

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