PII: S0032-3861(96)00827-0

Polymer Vol. 38 No. 11, pp. 2609–2614, 1997

0032-3861/97/$17.00 + 0.00

Study of the relationship between crack tip strain and crack propagation in polyurethane films using micro-*FT*i.r.

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(Received 17 June 1996)

In the present study, a series of polyether-urethane-ureas (PEUU) were selected for investigation of crack propagation behaviour under dynamic loading conditions. These model polyurethanes were synthesized by two-stage polymerization. The hard segments were composed of 4,4′-diphenyl methane diisocyanate (MDI) and ethylene diamine (EDA). The soft segments were polyglycols having different chemical structures and number average molecular weights of 1000 and 2000. Monitoring of the variation in molecular orientation at the crack tip region was accomplished using polarized *FT*i.r. microscopy. Molecular orientation of the four major functional groups, NH–, CH–, C=O, and C=C representing the domain, matrix, and interface region were measured as a function of strain for uncracked samples using the i.r.-dichroism technique. NH– and C=O functional groups present in the urea and correlated with the hard domains behaviour, exhibit a generalized orientation function–strain curve which was characterized by three regions. Region 1 was associated with an initial decrease in the orientation function at low strains followed by region 2, which is the minimum obtainable orientation, and region 3 a subsequent increase in the orientation function with an increase in strain. The molecular orientation was used to determine the real strain at the crack tip.

The strains at the crack tip for the pure (PEUU) were between 4 to 7 times higher than the applied strain. It was observed that higher soft segment molecular weights correlated with a larger strain at the crack tip. For the same soft segment molecular weights, polypropylene glycol (PPG) based PEUU showed higher strains at the crack tip. Therefore, the strain at the crack tip depends on chemical structure and the molecular weight of the soft segment. According to the strain data and the generally accepted deformation theory for PEUU elastomers, in all PEUUs, crack propagation occurred after the individual hard segments separated and oriented along the stretching direction. © 1997 Elsevier Science Ltd.

(Keywords: polyurethane; crack tip orientation; crack propagation; *FT*i.r. microscopy; orientation function)

INTRODUCTION

The various biomedical applications of polyurethanes makes knowledge of their mechanical properties and propensity for crack propagation under static and dynamic conditions a necessity for long and short term use. Numerous studies have focused on environmental stress cracking, a problem of great importance for medical device manufacturers[1–3]. While knowledge of crack growth resulting from a combination of environment and stress is necessary, a crack in a polyurethane elastomer could also grow as a result of static or dynamic loading. Early studies on fatigue behaviour of polyurethanes have provided a reasonable understanding regarding the effects of chemical structure and physiological environment[4–8], although none of these studies provided a molecular level interpretation of the crack propagation phenomena as a function of loading mode.

During loading the polymer molecules are subjected to orientation in a particular direction, usually in a direction parallel to the applied stress. The molecular orientation has a pronounced effect on the mechanical properties of polymers. Although not completely elucidated for notched samples, the molecular orientation at the crack tip appears to affect crack propagation. Thus, understanding of the molecular orientation at the crack tip appears to be essential in the elucidation of the interrelation between deformation, crack growth, and fracture properties of polymers.

In the present study, molecular orientation at the crack tip was determined for a series of polyether-urethane-ureas. Efforts were made to relate the molecular orientation at the crack tip to the chemical structure and molecular weight of the polyether segment. The corresponding strain at the crack tip was determined using the orientation function–strain plot. The molecular orientation and strain at the crack tip were related to crack propagation.

THEORETICAL BACKGROUND

Infrared dichroism and orientation function

The selectivity and absorptivity of interatomic bond vibrations can be used as a tool to measure molecular orientation. When polarized i.r. radiation is the source, the comparisons of the absorbances in each polarization

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plane can be used to determine the vibrational direction of atomic bonds. The comparison of the absorbances is known as i.r. dichroism. More specifically, i.r. dichroism is a method for measuring the orientation of the transition moment of a bond, not the bond itself. Because the transition moment direction is usually very close to the bond direction, polarized i.r. radiation is used to obtain information related to chemical bond orientation.

The ratio of the absorbances of plane polarized i.r. radiation in the parallel and perpendicular directions is the dichroic ratio

$$D_{12} = A_1/A_2 \qquad (1)$$

where D_{12} is the dichroic ratio with respect to the parallel (1) and perpendicular (2) directions, and A is the absorbance of polarized radiation in the specified directions.

The relationship between uniaxial orientation functions and dichroism was derived by Fraser[9,10]. The Hermans orientation function, f_H, can be expressed in terms of the dichroic ratio by

$$f_H = \frac{D^0_{12} - 1}{D_{12} + 2}\,\frac{D^0_{12} + 2}{D^0_{12} - 1} \qquad (2)$$

where $D_{12} = A_1/A_2$ and $D^0_{12} = A^0_1/A^0_2$. D^0_{12} are the dichroic ratio for a perfectly oriented sample. If α is the angle between the transition moment and the polymer chain backbone, D^0_{12} is given by

$$D^0_{12} = 2\cot^2\alpha \qquad (3)$$

Orientation measurement in polyether-urethane-ureas (PEUU)

Polyurethanes are known to have a domain-matrix morphology due to the chemical incompatibility of the segments. The domains consist predominantly of hard segments containing urethane (or urethane-urea) aggregates dispersed in the soft matrix which is essentially polyether segments. I.r. dichroism is a comparison between the parallel and perpendicular absorbances of a specific band. Thus, knowledge of the functional groups characteristic of the domains, matrix and the interfacial region is important in studying the effect of orientation on the morphological features. The four chemical groups that yield valuable information for orientation studies of polyurethanes are the N–H, C=O, CH_2 and C–O–C groups. The N–H and C=O groups are present in the urethane groups comprising the hard segments of both the domain and interfacial region. Most of the CH_2 groups and all C–O–C groups are present in the soft matrix. The relationships between absorption bands and specific regions of the polyurethane morphology are given in *Table 1*.

Table 1 I.r. absorption bands for molecular orientation of amine extended polyurethane elastomers

Absorption band, cm^{-1}	Assignments	Morphological region
3321	NH stretch (*h*-bonded)	Hard segment
2940	CH– stretch (asymmetric)	Soft segment
1732	C=O stretch in urethane	Hard/soft segment
1636	C=O stretch in urea	Hard segment
1112	C–O–C in polyether	Soft segment

EXPERIMENTAL

Materials

A series of polyetherurethane-ureas (PEUU) was selected for investigation of crack propagation behaviour under dynamic loading conditions. These model polyurethanes were synthesized by two-stage polymerization[11]. The hard segments were composed of 4,4′-diphenyl methane diisocyanate (MDI) and ethylene diamine (EDA). The soft segments were polyglycols having different chemical structures and number average molecular weight of 1000 and 2000.

Instrumentation

FTi.r. spectrometer. A Digilab FTS-40 *FT*i.r. spectrometer equipped with a UMA-300 i.r. microscope was used to collect the spectra. The *FT*i.r. microscope with the variable aperture facilitates the collection of spectrum from very small areas, such as, within a few microns from the very tip (front) of a growing or arrested crack, the so-called damaged or active zone. The polarizer employed for the micro-orientation studies was a Cambridge Physical Science IGP225, which was placed directly in the path of the beam.

Cyclic loading test machine. The automated fatigue/tensile tester described by Wong[12] and Kim[13] was used in these studies. Polyurethane films were mounted horizontally to allow for i.r. dichroism measurement on the focal plane of the i.r. microscope stage.

Orientation study at crack tip using FTi.r. microscopy

The *FT*i.r. microscope was set in transmission mode. The specimens with dimension of 2cm wide by 5cm long and a thickness of approximately 0.0254cm were placed under the visible/i.r. objective (32×) of i.r. microscope. Even at such a small thickness some absorption bands (e.g. CH stretching and C–O–C stretching) were often too intense. A polarizer was inserted at a right angle between the sample and the detector along the beam path. Crack tip orientation studies were carried out by using the aperture to focus on an area of approximately 30μm just ahead of the crack tip. The strains were given by using the automated cyclic tester. Parallel and perpendicular polarized spectra were collected after each film was stretched to the specific strain at a rate of 10% strain per second. The spectra were collected after 64 scans at a resolution of 4cm^{-1}. Background spectra collected for each polarized radiation were recorded before scanning the sample and used to obtain the spectra of the samples. Consequently, one set of spectra at a specific strain, i.e. a parallel and a perpendicular polarized spectrum, were acquired to achieve the orientation study under that strain, then the absorbances for the specific absorption band from perpendicular (A_1) and parallel (A_2) spectra were used to calculate the dichroic ratio, D. To minimize the effect of relaxation on the orientation data, the initial scanning time on the *FT*i.r. and the time for complete stretching were made to coincide. The samples were subjected to a total of one million cycles with intermittent pauses to measure crack growth and collect spectra.

RESULTS AND DISCUSSION

Synthesis

The model polyether-urethane-ureas (PEUU) prepared for this study are presented in *Table 2*. The sample nomenclature is based on the chemical nature and molecular weight of the soft segment. The soft segments used were polypropylene glycol (PPG), polytetramethylene glycol (PTMG), and polyethylene glycol (PEG). The molecular weights of these segments were 1000 and 2000. The molar ratio of the components is also given in *Table 2*.

Molecular orientation measurement of uncracked PEUU

An understanding of the relationship between cyclic loading and molecular deformation at the crack tip requires *a priori* knowledge of molecular orientation as a function of strain for uncracked samples. The molecular orientation of the four major functional groups (*Table 1*) representing the domain, matrix, and interface region were measured as a function of strain for uncracked samples by using the i.r.-dichroism technique. The orientation function dependence on applied strain for those functional groups are presented in *Figure 1*. The transition moment vectors of hydrogen bonded NH– stretching, CH– stretching, C=O stretching in urea and urethane groups, and C=C stretching in the aromatic rings were taken to be 90°, 90°, 78° and 0° to the chain axis, respectively[14,15].

The NH– and C=O functional groups present in urea and correlated with hard domains behaviour, exhibit a generalized orientation function–strain curve which is characterized by three regions. As shown in *Figure 1*, region 1 is associated with an initial decrease at low strains followed by region 2, which is the minimum in the curve, and region 3 a subsequent increase with increased strain.

Based on the segmented polyurethane deformation theory[16,17] the initial decrease correspond to a progressive movement of the domains to a position transverse to the applied load (*Figure 2*). At the minimum in the orientation function–strain curve it is assumed that all domains are transverse relative to the applied load. This minimum seems to depend on the chemical structure of the polyether segment. Upon further increasing strain, there is progressive disruption of the domains, the hard segments rotate to become aligned parallel to the direction of the applied load. The change in hard segment alignment from transverse to parallel relative to the loading direction is reflected in the change from negative to positive values of the orientation function for NH– and C=O functional groups in the urea moiety. For the purpose of this work, hard segment vertical alignment is considered to occur at positive values of the orientation function. The strain level at which the hard segment (–C=O) orientation function assumes positive values depend on molecular weight and chemical structure (i.e. flexibility and crystallizability) of the soft segment.

While the trend in the domain disruption is unclear, the hard segment alignment for PEG1000, PTMG1000, and PPG1000 is attained at strains of approximately 220%, 340% and larger than 500%, respectively. For polyetherurethane–ureas with polyether molecular weights of 2000, hard segment alignment for PTMG2000 and PPG2000 is attained at strains of approximately 430% and above 500%, respectively. This indicates that in these polyetherurethane–urea systems, the PPG based polyurethanes undergoes the highest strain prior to complete domain disruption. Since total strain in elastomeric systems is primarily a function of the chain flexibility and stress induced crystallization, the fact that a PPG segment undergoes the largest strain despite the relatively higher T_g (*Table 3*) is an indication that chain flexibility is not the major factor. Thermal studies on PEG2000 and PTMG2000 exhibited crystalline melting transitions[18]. Thus, the ability of the polyether segments to pack closely or possibly crystallize seems to be more important in determining the strain at which domain disruption and segmental orientation occurs. The observation of crystalline melting transitions for both PEG2000 and PTMG2000 provided support for the relationship between development of crystallinity and the critical strain for segmental orientation.

Methylene (CH_2^-), which can be used to characterize the behaviour of the soft segments, exhibited monotonic increases in the orientation functions with increased strain (*Figure 1*) for most PEUU. All values for the orientation function of methylene groups were positive indicating the ease with which the polyether (PPG, PTMG and PEG) segments tended to align, parallel to the applied stress. The orientation function for the polyether $-CH_2$ in the PPG based polyurethane is constant, close to zero over the entire strain range. The relative constant value, close to zero, arises from the rapid relaxation of a polyether segment whose motion is not encumbered by close packing or crystallization. In contrast, the orientation function for the polyether $-CH_2$ in the PTMG based polyurethanes–urea showed a monotonic increase over the same strain range. The increase is consistent with the ability of these chains to pack closely, even to crystallize.

The free and hydrogen bonded C=O in the urethanes which are located at the interface also showed a monotonic increase in the value of the orientation function (*Figure 1*). All the values for the orientation function for the C=O are positive. This behaviour indicates that both the free and hydrogen bonded C=O can coexist in the same segment and are easily oriented parallel to the axis of the applied stress. The similarity in behaviour of the free and hydrogen bonded carbonyl groups can be understood by realizing that urethane segments located at the interface are not part of a domain and as such, carbonyl groups may be hydrogen bonded to another single hard segment. Two hydrogen bonded hard segments in an environment of flexible polyether segments should orient along the axis of applied stress much easier than in an environment of rigid hard segments.

Table 2 Composition and hard segment contents of synthesized PEUU

Sample name	Soft segment type	Molar ratio (MDI : OL : CE)[a]	Hard segment content, wt%
PTMG1000	PTMG (M_n : 1000)	2 : 1 : 1	35.9
PTMG2000	PTMG (M_n : 2000)	2 : 1 : 1	21.9
PPG1000	PPG (M_n : 1000)	2 : 1 : 1	35.9
PPG2000	PPG (M_n : 2000)	2 : 1 : 1	21.9
PEG1000	PEG (M_n : 1000)	2 : 1 : 1	35.8

[a] MDI: 4,4′-diphenyl methane diisocyanate; OL: polyglycol; CE: chain extender (ethylene diamine)

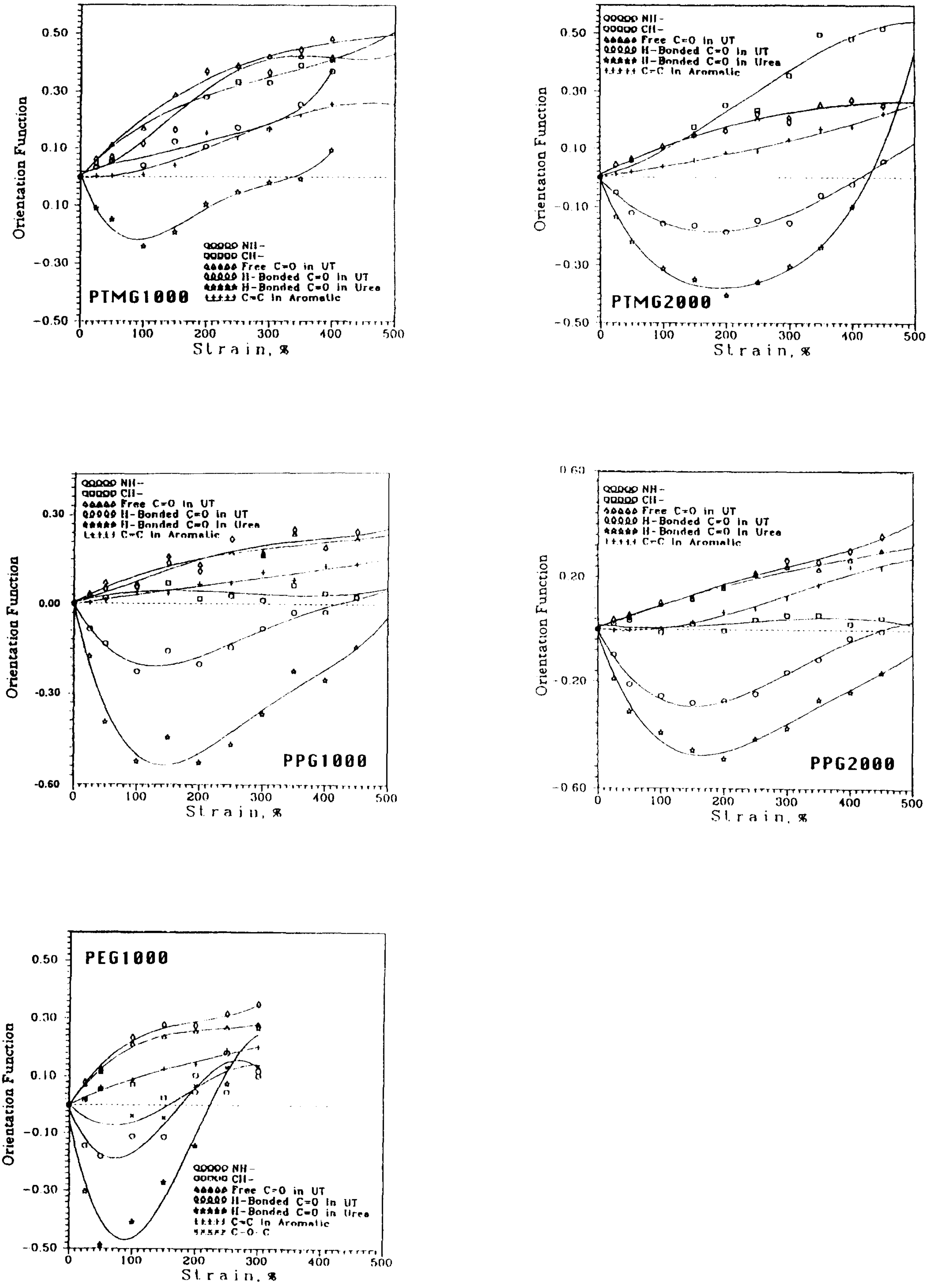

Figure 1 Orientation function dependence on applied strain for functional groups

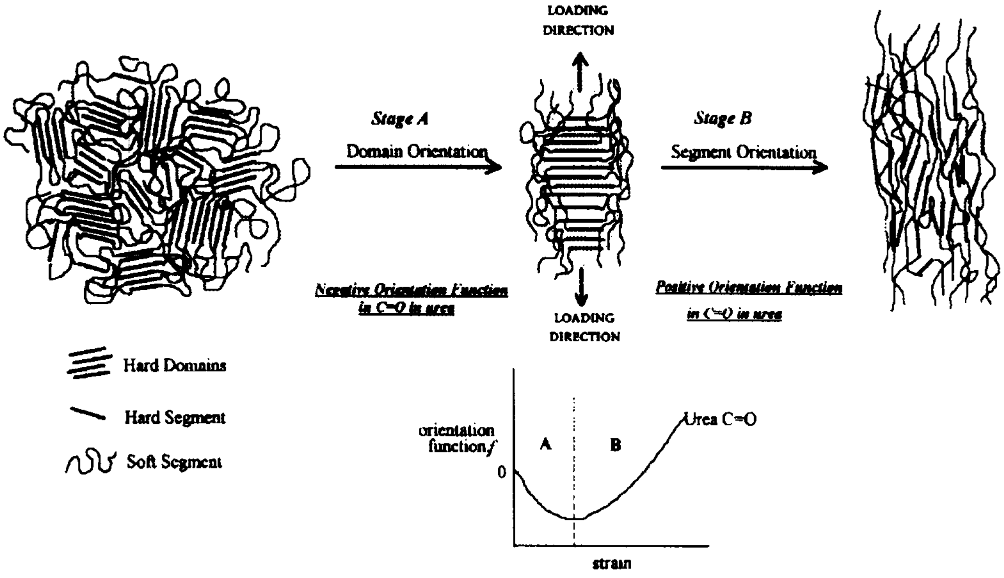

Figure 2 Generally accepted deformation theory for poly(ether-urethane-urea) (PEUU) and typical orientation function curve of urea C=O with changing strain

Table 3 Soft segment T_g and critical strain for PEUU

Sample name	Soft segment T_g (°C)	Strain at f_H (min)	Strain at $f_H > 0$
PTMG1000	−30	100	340
PTMG2000	−40	200	430
PPG1000	0	140	> 500
PPG2000	−35	160	> 500
PEG1000	−15	90	220

The orientation function–strain curves of the –NH for PEG1000, PPG1000 and PPG2000 are similar. While inspection of the orientation function–strain curve for PTMG1000 and 2000 reveals pronounced differences between the position of the minimum and strain at which the orientation function becomes positive. The value of the orientation function for –NH groups in PTMG2000 is initially negative and at higher strains becomes positive (*Figure 1*). This behaviour is different to PTMG1000 where the orientation function for the –NH group is always positive. The difference in behaviour may be attributed to an increase in molecular weight of polyether segment leading to better phase separation.

Molecular orientation measurement at the crack tip

Fatigue crack propagation begins when the length of a crack reaches a critical value. Crack propagation is a completely localized and relatively slow process when compared with failures from tensile or impact type tests. Theoretically, crack tip analysis has been well established for linear elastic materials using stress field analysis. By the same theoretical background, the stress field analysis for non-linear elastic materials showing a larger plastic deformation near crack tip region is not easily characterized due to a large plastic zone and time dependent viscoelastic properties. Fortunately, during polymer deformation, molecular chains or any microscopic structure such as a crystalline phase or other incorporated entities tend to orient in a unique way depending on the applied strain and polymer structure. Thus, the deformation state just prior to the crack growth, i.e. the critical deformation (or orientation) condition at the damaged (or action) zone can be obtained from the molecular orientation. In this research, orientation behaviour of major functional groups was taken at the crack tip area in order to estimate the strain level of the crack tip under 50% applied strain. The strain at the crack tip was determined by combining the molecular orientation at the crack tip and the orientation function changes with respect to strain for uncracked samples.

The orientation function at the crack tip was first determined using the urea carbonyl (–C=O) and the polyether methylene ($-CH_2$) in each sample. Then, strains at the crack tip area were estimated by interpolation using the orientation functions vs per cent strain plots given in *Figure 1*. The hydrogen bonded urea C=O group was selected because the changes in the orientation function are large enough to permit interpolation of the strain from the orientation function–strain plot. The orientation function–strain curve of the C=C in the aromatic rings were used to calibrate the urea carbonyl because it was positive and relatively linear with increased elongation. The C=C in the aromatic rings which only existed in the hard segments permitted the determination of whether the strain obtained from the orientation function of the urea C=O exceeded the minimum point on the orientation function curve. *Table 4* shows the percent (%) strain at the crack tip for the various PEUU. Generally, the strain at the crack tip using the orientation function of urea C=O is about 4–7 times higher than the applied strain. As expected, the crack tip area domains (or hard segments) under strain have a higher orientation compared to those removed from the active areas or damaged zone ahead of the crack tip.

It was found that all strain approximated from the CH– orientation function of the soft (polyether) segments were considerably less than the strains obtained from the hydrogen bonded urea C=O in the domains. This discrepancy is due exclusively to the fact that polyether segments undergo a faster relaxation than the hard domain.

It is clear that higher soft segment molecular weight

Table 4 Estimated strain at the crack tip from orientation measurements at 50% applied strain

Sample	Crack propagation	% strain from C=O in urea	% strain from CH
PTMG1000	Yes	195	140
PTMG2000	No	330	135
PPG1000	Yes	315	n.a.
PPG2000	No	350	n.a.
PEG1000	Yes	185	55

leads to a larger percent strain at the crack tip region. This means that deformation at the crack tip region of PTMG2000 and PPG2000 are larger than in PTMG1000 and PPG1000, respectively. All PPG based PEUU exhibited a higher percent strain at the crack tip than did PTMG or PEG based PEUU despite their comparatively higher T_gs. These results are consistent with the observation from the uncracked samples and can be explained by a higher chain mobility of PPG segments. The lower strain values observed for PTMG and PEG based PEUU is due to a reduction in chain mobility resulting from the close packing and/or crystalline phase. For PEUU's having the same polyether segment, a lower strain at the crack tip was associated with crack propagation.

Since all the strains listed in *Table 4* are greater than f_H (min), the deformation theory of segmented polyurethanes[6,16,17] predicts that segmental orientation will be dominant over the domain orientation in the PEUU (see *Figure 2*). This means that prior to crack propagation, most of the domains in the damaged zone have already been disrupted and the hard segments are tending to orient parallel to the stretching direction. Therefore, crack propagation apparently required that segmental orientation exist along the stretching direction perpendicular to the crack growth direction.

Finally, the results indicate that FCP behaviour of model PEUU can be strongly correlated with the percent strain at the crack tip. The percent strain at the crack tip of PEUU having no crack propagation is higher than those having crack propagation. Thus, as the polymer chains at the crack tip are able to undergo higher strains, the susceptibility to crack growth decreases.

CONCLUSIONS

Direct monitoring of the variation of molecular orientation at the crack tip region can be accomplished by using polarized *FT*i.r. microscopy. The molecular orientation can be used to determine the real strain at the crack tip area. The strains at the crack tip for the pure PEUU were between 4 to 7 times higher than the applied strain. It was observed that higher soft segment molecular weight correlated with larger strain at the crack tip. For the same soft segment molecular weights, PPG based PEUU showed the highest strains at the crack tip. Therefore, the strain at the crack tip depends on the chemical structure and molecular weight of the soft segment.

According to the strain data and the generally accepted deformation theory for PEUU elastomers, in all PEUUs, crack propagation occurred after the individual hard segments were separated and oriented along the stretching direction.

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