

Fracture behaviour of thin polyimide films

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The deformation and fracture behaviour of aromatic polyimide films (BPDA-PDA, PMDA-ODA, PMDA-BAPB and PMDA-BAPP) was investigated and related with local molecular order. It was found that local molecular order, i.e. bundles of parallel-packed main chains dominated the deformation and fracture behaviour of polyimide films. The fracture behaviour of respective polyimides was heterogeneous over thickness in films with low degree of local molecular order, while this phenomenon disappeared in films with high degree of local molecular order. The tear energy showed maximum value as the degree of local molecular order increased. Also, the deformation behaviour of PMDA-BAPP films with low degree of local molecular order showed a combination of crazing and shear yielding. Other polyimide films with high degree of local molecular order showed only shear yielding in single-edge notched tension test. © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: polyimide films; local molecular order; deformation mechanism)

INTRODUCTION

Aromatic polyimides have been widely used in aerospace and microelectronics industries, due to their excellent thermal stability, mechanical and electrical properties. Polyimides also have been a wide variety of use as coatings, adhesives, films and fibre. In the film application deformation and fracture behaviour is of importance.

However, little attention has been drawn on the mechanical behaviour of polyimide films and most studies on mechanical properties of polyimide films are tensile behaviour^{1,2}. Recently the deformation and fracture behaviour of polyimide films are reported^{3–9}. Argon *et al.*⁶ examined the deformation of polyimide films and correlated activation volume with deformation mechanism. They indicated that activation volume can be used to estimate qualitatively plastic deformation mechanism, i.e. microcavitation (0.1 μm in size) and shear band formation. They showed that as activation volume increases shear band disappears and microcavity appears. Pater *et al.*⁷ investigated the deformation mechanism of various polyimide films and they explained the deformation mode in terms of crystallinity. They showed that ordered polyimides display only diffuse shear yielding, while fully amorphous polyimides exhibit combined crazing and shear yielding. Hinkley *et al.*⁹ investigated the deformation mechanism of polyimide blends consisting of thermoplastic polyimide LARC-TPI and addition type polyimide PMR15. They show that PMR15 is deformed via shear yielding due to high cross-link density and deformation mechanism is changed from shear yielding to crazing with addition of LARC-TPI.

It is important to understand the mechanical properties of polymers on a molecular level. There have been

theoretical attempts to describe the deformation of various polymers from molecular level like entanglement density¹⁰. Most polyimides except thermoplastic polyimides such as Ultem and LARC-TPI are insoluble and infusible, so it is difficult to describe the physical properties of polyimides in terms of molecular parameters. Recently the mechanical behaviour of aromatic polyimides can be explained by local molecular order (molecular packing or aggregation) consisting of bundles of parallel-packed main chains¹¹, which is formed by charge transfer interaction. The degree of local molecular order is affected by chemical structure and heat treatment. It is known that charge transfer interaction was determined by electron affinity of dianhydride and ionization potential of diamine¹². Also it is affected by imidization temperature and local molecular order is well formed at higher imidization temperature¹¹.

In this study, we have investigated the deformation and fracture behaviour of polyimide films with different degree of local molecular order, using various polyimides. The degree of local molecular order was controlled by imidization temperature. And we studied the relationship between fracture behaviour and degree of local molecular order.

EXPERIMENTAL

Table 1 illustrates the monomers which were used in synthesis of polyimides. The dianhydrides were purchased from Daicel Chemistry Co. and were used after drying at 180°C. The diamines were supplied by Wakayama Seiko Kogyo Co. and were used after drying at 50°C under vacuum. *N*-Methyl-pyrrolidinone (NMP) was vacuum distilled after stirring over calcium hydride. The poly(amic acids) were prepared by condensation polymerization. The equimolar dianhydride was added gradually to the diamine in NMP solution with stirring. The reaction was allowed to proceed for 4 h

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Table 1 Monomers used for synthesis of polyimides

Monomer	Dianhydride	Diamine
BPDA-ODA		
PMDA-ODA		
PMDA-BAPB		
PMDA-BAPP		

BPDA-PDA: 3,4,3',4'-Biphenyltetracarboxylic dianhydride-*p*-phenylenediamine

PMDA-ODA: Pyromellitic dianhydride-oxydianiline

PMDA-BAPB: Pyromellitic dianhydride-1,4-bis(4-aminophenoxy)benzene

PMDA-BAPP: Pyromellitic dianhydride-2,2-bis[4-(4-aminophenoxy)phenyl]propane

in a N_2 atmosphere and the reaction temperature was kept below $40^\circ C$. The viscosity of solution increased rapidly. To control viscosity of the reaction mixture, 0.15 mol% excess of dianhydride was added to the reaction mixture and it was heated at $80^\circ C$ for 1 h. The solid content was 15 wt%. After cooling, the poly(amic acid) solution was stored in the refrigerator.

The poly(amic acid) solutions were cast on the slide glass using doctor blade. The cast films were dried at $80^\circ C$ for 1 h on a hot plate. They were heated to imidization temperature at a heating rate of $7^\circ C \text{ min}^{-1}$ and then were cured under nitrogen flow. The imidization condition is $200^\circ C \times 3 \text{ h}$, $250^\circ C \times 2 \text{ h}$, $300^\circ C \times 1 \text{ h}$, $350^\circ C \times 1 \text{ h}$ or $400^\circ C \times 1 \text{ h}$, respectively. After imidization, the polyimide films were slowly cooled down and removed from slide glass. The thickness of the film was around $30 \mu\text{m}$.

The degree of local molecular order was estimated from the packing coefficient proposed by Slonimskii. Packing coefficient, K was expressed as¹³

$$K = V_{\text{sp}}/V_{\text{exp}} = dN_A \sum n_i V_i / M \quad (1)$$

where V_{sp} is specific van der Waals volume, V_{exp} is experimental volume, d is density, N_A is Avogadro's number, n_i is number of contributors, V_i is contribution of i th atom or group to V_{sp} and M is molecular weight of repeating unit. The specific van der Waals volume is defined as the volume occupied by the molecules, which is impenetrable to other molecules at ordinary temperature¹⁴. The specific van der Waals volume is assumed to be bounded by the outer surface of a number of interpenetrating spheres. The radii of spheres are assumed to atomic radii for the element involved and the distance between centres of the sphere are the bond lengths for calculation. The contribution of a given atom A with radius R to specific van der Waals volume is then given by

$$V_{\text{sp},A} = N_A \left[4\pi R^3/3 - \sum \pi h_i^2 (R - h_i/3) \right] \quad (2)$$

$$h_i = R - l_i/2 - R^2/2l_i + r_i^2/2l_i$$

where r_i is the radius of atom i covalently bonded to A

and l_i is bond distance between A and i . According to this definition, volume contribution $V_{\text{sp},A}$ of the atom is not constant because of the surrounding atoms¹⁴.

In this study, the specific van der Waals volume was determined by the summation of the van der Waals volume of composing structure unit calculated by Slonimskii¹³. The density was measured using density gradient column consisting of cyclohexane and carbon tetrachloride at $30^\circ C$.

The tear energy was determined by the trouser tear test. Specimens (15 mm width, 70 mm length) were cut from films. Tests were conducted with 0.5 mm min^{-1} cross head speed at room temperature using an Instron machine (Model 4202). Tear path width was measured using an optical microscope and tear energy was calculated using equation (3)

$$G_C = 2F/t \quad (3)$$

where G_C is tear energy, F is tear force and t is tear path width. Tear energy was determined using eight specimens and taken as an average value.

Torn surface was examined by scanning electron microscopy (SEM) (Hitachi S-570) after gold coating. In particular, scanning electron micrographs were obtained from both the air side and glass side which had been in contact with poly(amic acid) film during imidization. The polyimide strips (6.4 mm width) were cut with a razor blade to create the edge notch and were tested to failure in a miniature tensile system installed on the stage of an optical microscope. The cross head speed was 0.5 mm min^{-1} and the crack tip region was examined by optical microscope. A dynamic mechanical test at 1 Hz in tensile mode between $100^\circ C$ and $500^\circ C$ was conducted using Polymer Laboratories DMTA apparatus. Also tensile behaviour was determined at a cross head speed of 5 mm min^{-1} using an Instron machine.

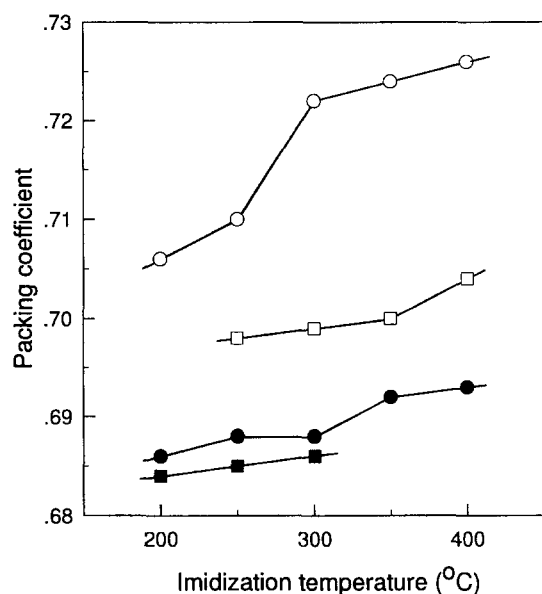
RESULTS AND DISCUSSION

Packing coefficient

The mass densities of polyimides as a function of imidization temperature are shown in Table 2. The densities of polyimides were found to increase slowly as

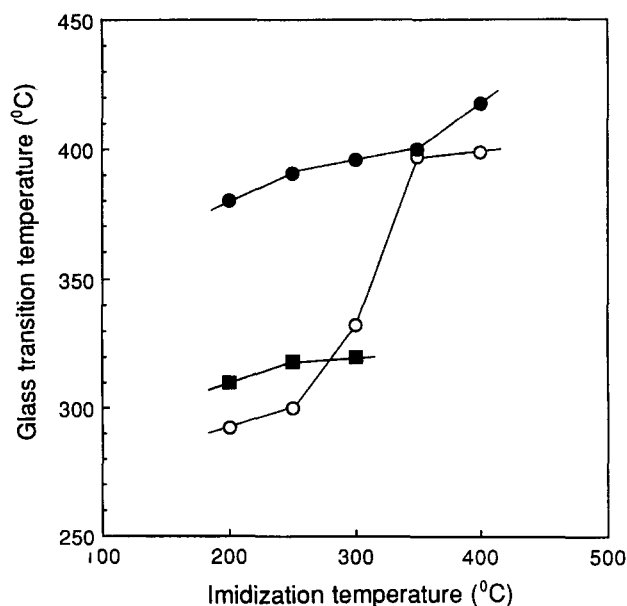
Table 2 Mass densities of polyimide films as a function of imidization temperature

Polyimide	Imidization temperature (°C)				
	200	250	300	350	400
BPDA-PDA	1.4330	1.4409	1.4646	1.4693	1.4744
PMDA-ODA	1.4088	1.4130	1.4135	1.4204	1.4210
PMDA-BAPB		1.4111	1.4125	1.4158	1.4242
PMDA-BAPP	1.3130	1.3163	1.3169		

**Figure 1** Packing coefficient as a function of imidization temperature: (○) BPDA-PDA, (●) PMDA-ODA, (□) PMDA-BAPB, (■) PMDA-BAPP

imidization temperature increased. These results were consistent with previous work and attributed to an increase in ordering or packing of the polyimide chains¹⁵.

Figure 1 shows the dependence of the packing coefficient on imidization temperature. As imidization temperature increased packing coefficient increased. In the case of BPDA-PDA, a significant increase in packing coefficient was obtained over 300°C imidization temperature. It was reported that imidization reaction is completed at 200°C for 1 h¹⁶ and local molecular order (i.e. polyimide chains are densely packed and have fully extended local conformation) is formed by intermolecular interaction on annealing polyimide film above 200°C^{11,17}. Therefore in this study, imidization reaction was almost completed in all samples and the increase in packing coefficient with imidization temperature is attributed to the formation of local molecular order. These results were ascertained by determination of the glass transition temperature using a dynamic mechanical test. It was found that as imidization temperature increased glass transition temperature increased in Figure 2. This phenomenon is a result of formation of local molecular order and is consistent with previous work^{11,18}. The glass transition temperature of PMDA-BAPB could not be measured between 100°C and 500°C. It was an unexpected result, considering chemical structure of PMDA-BAPB with two flexible ether linkages. It is reported that PMDA-BAPB do not show glass transition temperature¹⁹.

**Figure 2** Glass transition temperature of polyimide films as a function of imidization temperature: (○) BPDA-PDA, (●) PMDA-ODA, (■) PMDA-BAPP

As shown in Figure 1, the dependence of formation of local molecular order on imidization temperature, dK/dT increased as the rigidity of polyimide backbone increased. It is well known that the more rigid polyimide chains form the higher degree of local molecular order²⁰. So, rigid BPDA-PDA showed high packing coefficient, whereas PMDA-BAPP with bulky side groups showed low packing coefficient due to restricted chain-chain packing. This relationship between chemical structure and packing coefficient is in good agreement with Numata's study²¹. According to Slonimskii *et al.*¹³, most amorphous polymers have an approximately identical value of packing coefficient, of which the average value is 0.681. Therefore PMDA-BAPP films are in an amorphous state even at high imidization temperature, 300°C. However, PMDA-BAPB with two flexible ether linkages showed higher packing coefficient than PMDA-ODA with single ether linkage. Also PMDA-BAPB did not show a glass transition temperature. The reason for this phenomenon is not yet clear.

Tear energy

Figure 3 shows the variation of tear energy as a function of packing coefficient. All samples exhibit a similar trend, i.e. as packing coefficient increased the tear energy increased up to maximum value and then decreased. In the case of PMDA-BAPP thermal degradation occurred at 350°C, so tear energy decreased rapidly. Tensile behaviour shows the same tendency as tear energy. In Figure 4, as packing coefficient increased tensile energy to break increased up to maximum value and then decreased. Packing coefficients at which tensile energy to break shows the maximum value were the same as those of tear energy in all samples. These phenomena are attributed that tear energy is the energy required to extend the sample to its maximum elongation and it depends on the shape of the stress-strain curve²². Therefore the tear energy showed maximum value when the film had a maximum elongation which was

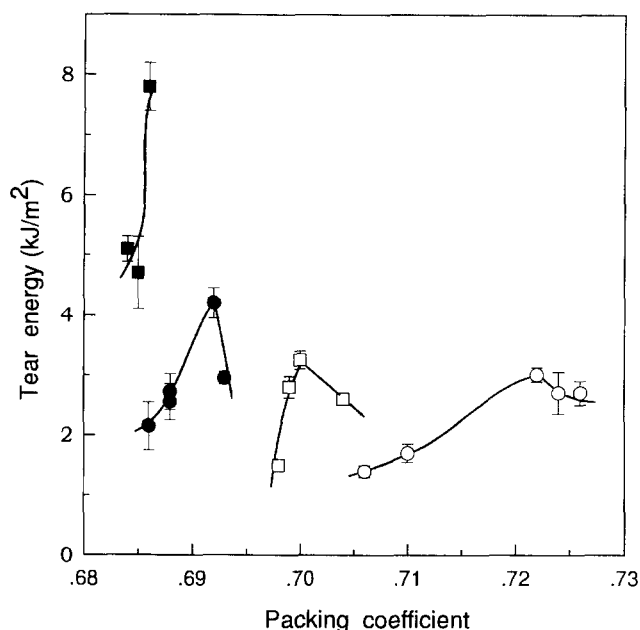


Figure 3 Tear energy as a function of packing coefficient: (○) BPDA-PDA, (●) PMDA-ODA, (□) PMDA-BAPB, (■) PMDA-BAPP

confirmed by tensile behaviour. Elongation at break in tensile behaviour is shown in *Figure 5*. For example, elongation at break was around 20% in PMDA-ODA film imidized at 200°C. As packing coefficient increased elongation increased up to around 85% in film imidized at 350°C and then decreased rapidly. Thus tear energy, tensile energy to break and elongation at break showed maximum at the same packing coefficient, i.e. the same imidization temperature in respective polyimide films. However, the tensile energy to break and elongation at break of PMDA-BAPB are very low compared with tear energy and this result may be attributed to the difference in test speed. It was supposed that the effect of degree of local molecular order on the mechanical behaviour is analogous to that of crystallinity in semicrystalline polymers. Semicrystalline polymers sometimes exhibit small extension to failure at low crystallinity, while polymers tend to yield and fracture energy increases when crystallinity changes from low to high. However, polymers become brittle at very high crystallinity²³. Although the local molecular order is different from crystals in size, local molecular order in polyimide films might act like crystals in semicrystalline polymers⁷. So the polyimide films with low degree of local molecular order exhibited small elongation, while polyimide films tended to yield and tear energy increased as degree of local molecular order increased. However, the polyimide films with very high degree of local molecular order became brittle and tear energy decreased.

Failure process

Torn surface of BPDA-PDA imidized at 250°C was very different in appearance for both sides of films (*Figure 6a*). *Figure 6a* is magnified in *Figure 7*. The torn surface of the glass side showed rough texture (*Figure 7a*), whereas the torn surface of the air side showed fracture surface like brittle fracture of glassy polymers (*Figure 7b*). However, torn surface of BPDA-PDA film imidized at higher temperature, 350°C (*Figure 6b*), was

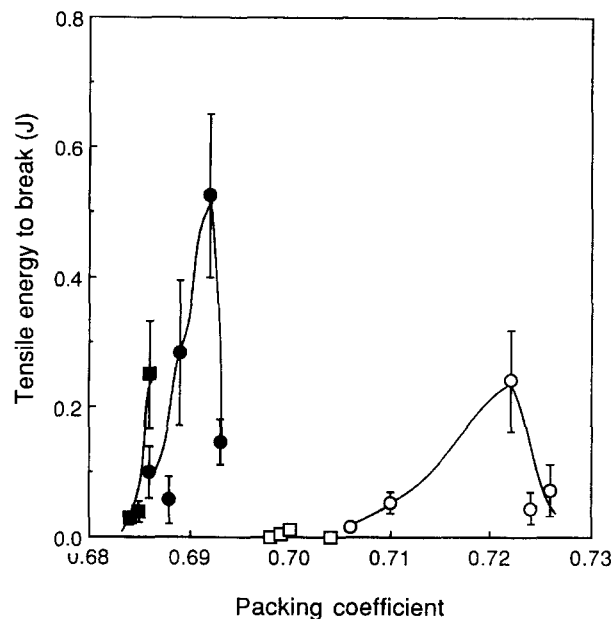


Figure 4 Tensile energy to break of polyimide films as a function of packing coefficient: (○) BPDA-PDA, (●) PMDA-ODA, (□) PMDA-BAPB, (■) PMDA-BAPP

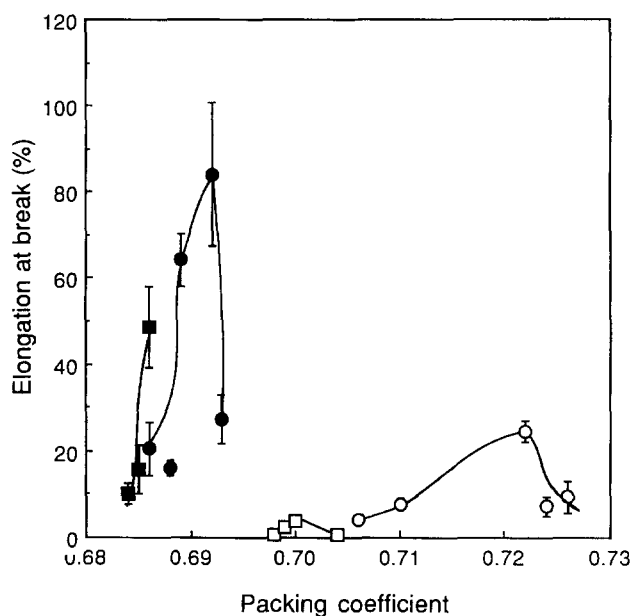


Figure 5 Elongation at break of polyimide films as a function of packing coefficient: (○) BPDA-PDA, (●) PMDA-ODA, (□) PMDA-BAPB, (■) PMDA-BAPP

different from that of films imidized at 250°C. The torn surface showed homogeneous rough texture over all thicknesses compared with torn surface of films imidized at 250°C. The torn surface of PMDA-ODA films imidized at 200°C was similar to that of BPDA-PDA imidized at 250°C, while the torn surface of PMDA-ODA imidized at 350°C showed unstable crack propagation and large deformation by yielding at the crack tip. So tear energy was high and heterogeneous fracture surface over thickness disappeared (*Figure 8a*). However, the torn surface of PMDA-ODA cured at 400°C showed a rather smooth fracture surface (*Figure 8b*) like that of glassy polymers and unstable crack propagation

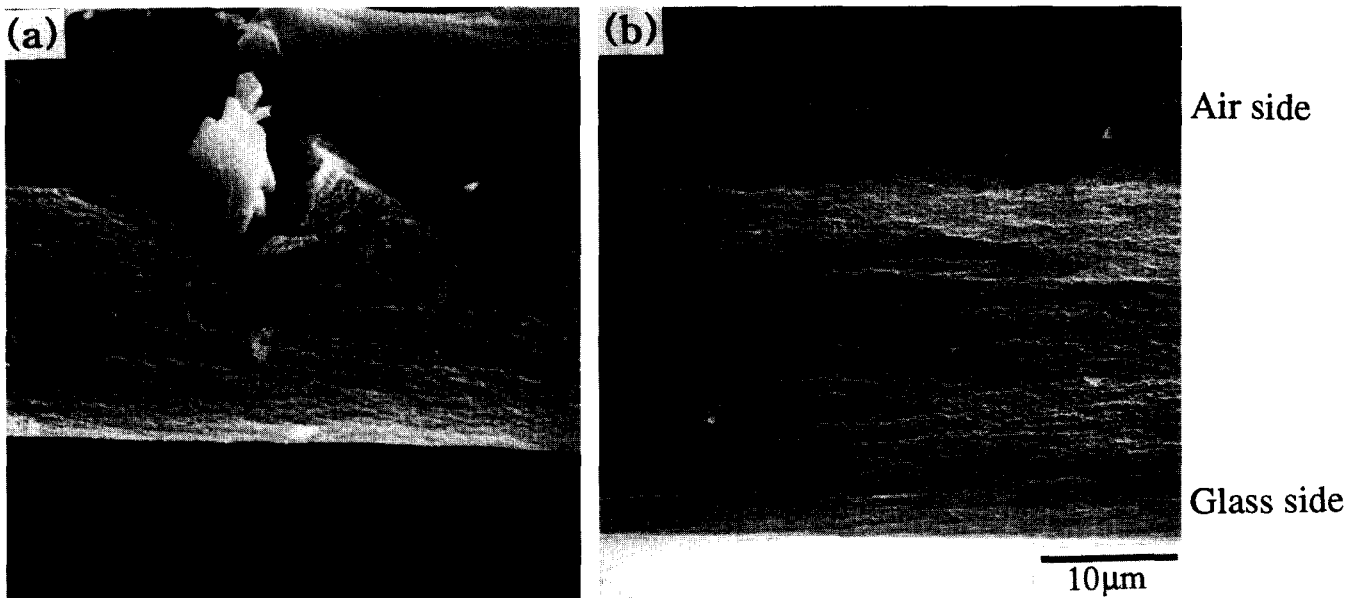


Figure 6 Scanning electron micrographs of torn surface of BPDA-PDA films imidized at: (a) 250°C, (b) 350°C

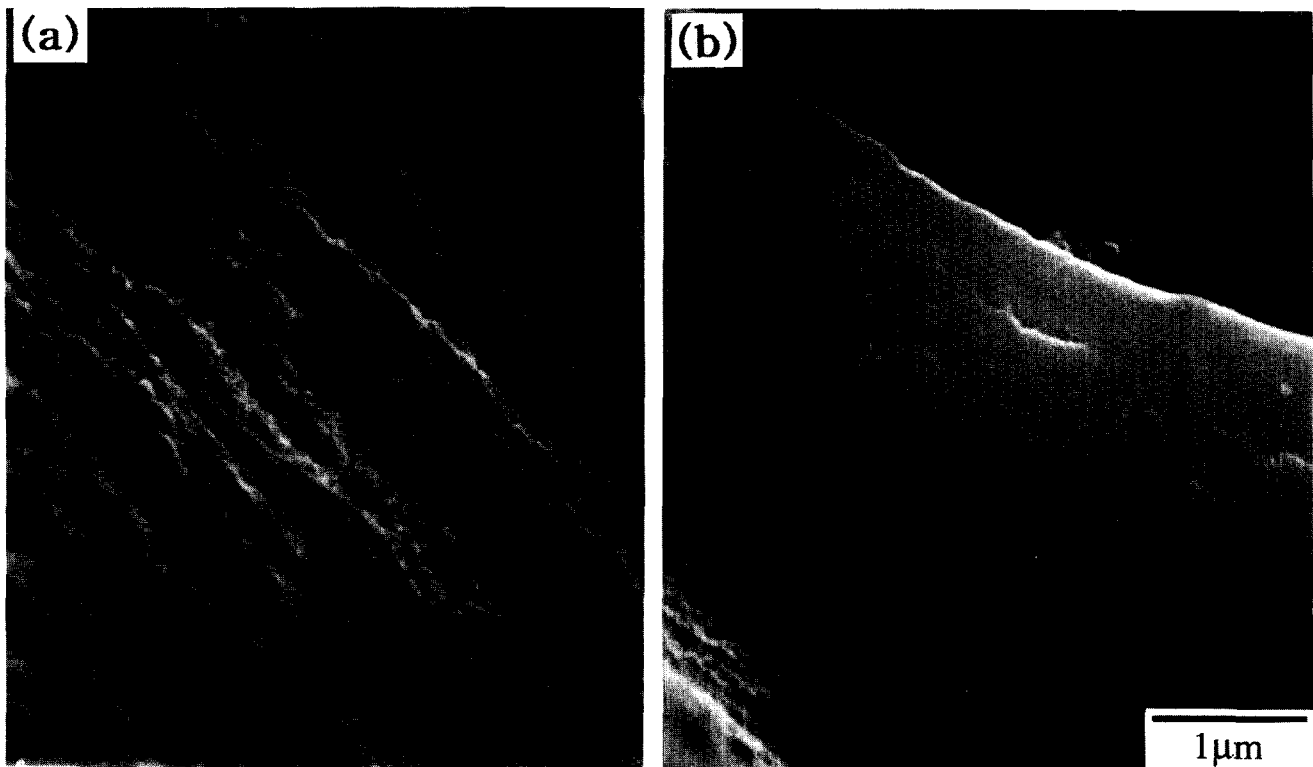


Figure 7 Higher magnification of Figure 6a: (a) glass side, (b) air side

disappeared and tear energy decreased. Thus the observation of scanning electron micrographs of torn surface is consistent with tear energy results.

The reason why fracture behaviour is different for both sides of films imidized at low temperature and homogeneous fracture over thickness occurred in films imidized at high temperature is as follows. The local molecular order of polyimide is strongly affected by heat treatment and chain orientation^{11,17}. Curing polyimide films on substrate, the polyimide chains become a planar arrangement in films due to interaction of substrate and polyimide chains, i.e. chain segments adsorbed on the

surface of substrate have a planar orientation and form local molecular order consisting of bundles of parallel-packed main chains. It is known that when imidization temperature is high completely planar ordering was formed to thickness of 20 μm from substrate in polyimide films and partially planar order was formed to thickness of 40 μm ²⁴. At low imidization temperature, local order of molecular chains is mainly distributed in films of glass side because of chain orientation due to interaction between glass substrate and polyimide chains. Therefore, for films imidized at low temperature films of glass side showed rough texture during fracture due to local

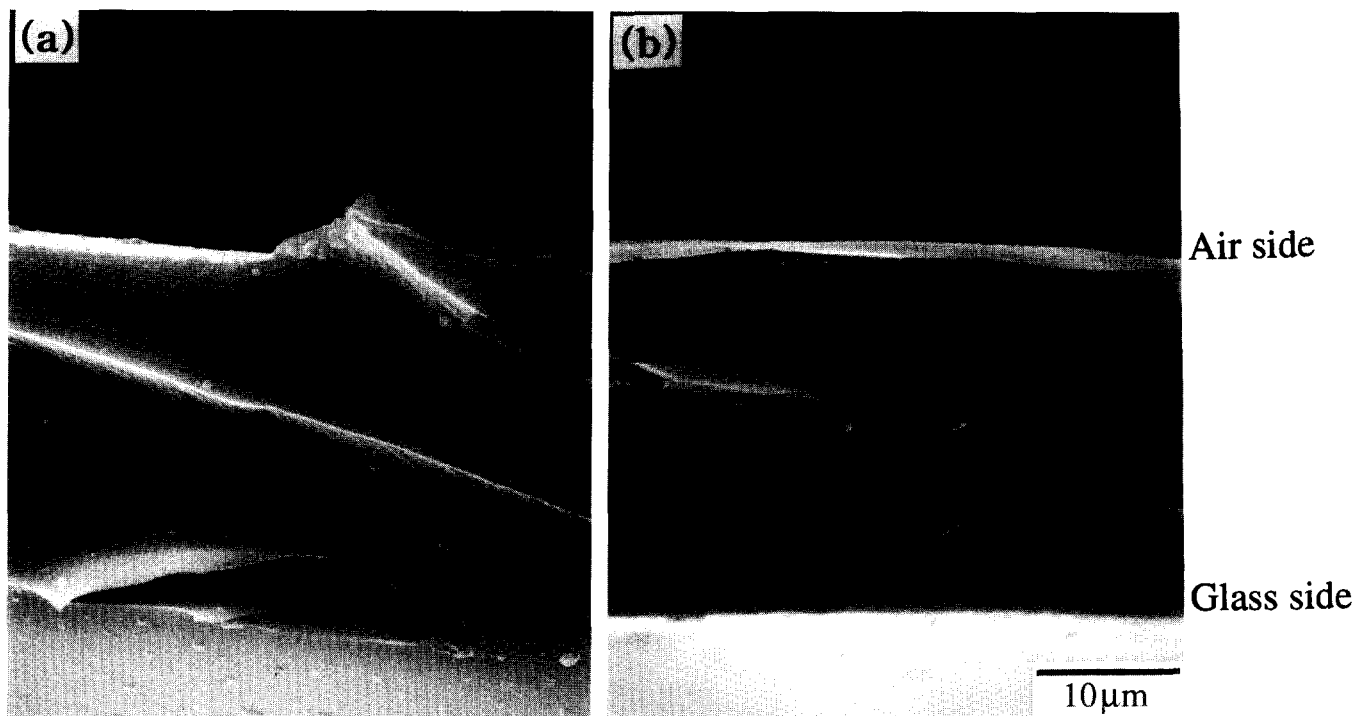


Figure 8 Scanning electron micrographs of torn surface of PMDA-ODA films imidized at: (a) 350°C, (b) 400°C

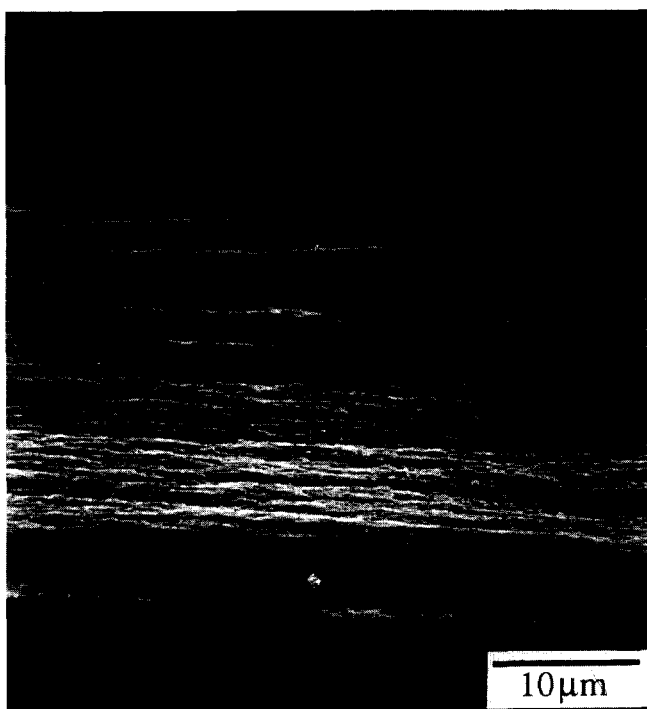


Figure 9 Scanning electron micrograph of torn surface of BPDA-PDA film imidized in a free standing form at 250°C



Figure 10 Scanning electron micrograph of torn surface of PMDA-BAPP film imidized at 300°C

molecular order, whereas films of air side were almost in an amorphous state and brittle fracture occurred. In *Figure 6a*, torn surface showed rough texture to thickness of about 20 µm and it was consistent with thickness over which completely planar order is formed by only interaction between substrate and polyimide chains²⁴. It was known that local molecular order of polyimide films is well formed at high imidization temperature due to charge transfer interaction¹¹. At high imidization

temperature, local molecular order may be well formed even at film of air side by strong charge transfer interaction between chains. Of course, local molecular order is well formed at film of glass side by not only charge transfer interaction but interaction between substrate and polyimide chains. According to previous work²⁴, local molecular order is formed to a thickness of

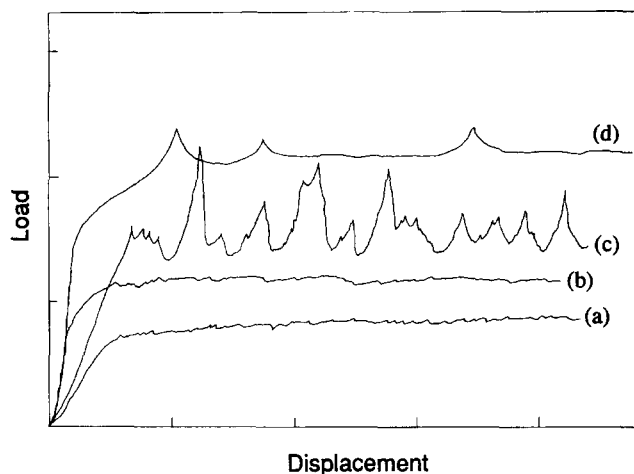


Figure 11 Typical load-displacement behaviour of polyimide films showed maximum tear energy in trouser tear test: (a) BPDA-PDA, (b) PMDA-BAPB, (c) PMDA-ODA, (d) PMDA-BAPP

40 μm . Therefore packing coefficient increased with imidization temperature, as described previously. It was supposed that local molecular order formed at films of air side may affect fracture behaviour of polyimide films. So, heterogeneous fracture behaviour of polyimide films imidized at high temperature disappeared. This result was confirmed by the other deformation experiment using polyimide films imidized in a free standing form. The BPDA-PDA poly(amic acid) film dried at 80°C for 1 h was removed from the slide glass and fixed on a metal spacer in a free standing form and then imidized at 250°C. As shown in Figure 9, the torn surface of BPDA-PDA film imidized by the above method showed homogeneous fracture surface over all thicknesses like that of film imidized at 350°C on substrate. In this case polyimide chain became a planar arrangement over all thickness in action of metal spacer and local molecular order was formed in the range of thickness even at low imidized temperature.

Considering chemical structure, the tear energy increased as the flexibility of polyimide backbone increased. This can be understood on the basis of chain mobility of polyimide backbone. PMDA-BAPP is quite a flexible structure and showed low yield stress in tensile behaviour. So, tear energy was the highest in samples due to large plastic deformation at crack tip (Figure 10). As mentioned previously, PMDA-ODA film imidized at 350°C showed unstable stick/slip propagation (Figure 11). It is evident that PMDA-ODA yielded at the crack tip and showed higher tear energy than BPDA-PDA and PMDA-BAPB. On the other hand, BPDA-PDA exhibited high yield stress and PMDA-BAPB fractured before yielding in tensile behaviour. These polyimide films

showed stable crack propagation and small deformation in yielding. Therefore these polyimide films show low tear energy. Tensile yield stress is shown in Table 3. These results are in good agreement with the relationship between yield stress and type of crack propagation²⁵. It was reported that for resins with high yield stress (>100 MPa), plasticity at crack tip is limited and stable crack propagation was observed. However, for resins with low yield stress, materials at the crack tip plastically flow to cause crack arrest²⁵. These phenomena were also observed in polyimides²⁵.

Optical micrographs in a single edge notched tension test were shown in Figure 12. PMDA-BAPP showed a thin necked region bordered by a dense line (Figure 12a). Also many crazes appeared at distant region from crack tip perpendicular to tensile direction (Figure 12b). The overall deformation appearance was similar to that observed in LARC-TPI, etc.^{5,9}. In the case of PMDA-ODA (Figure 12c), there was no evidence that craze occurred at the crack tip. A necked zone at the crack showed a coloured band when viewed with cross polarizers. This birefringent zone remained after load is removed. This phenomenon indicated that deformation occurred via yielding at the crack tip⁵. The deformation behaviour of BPDA-PDA and PMDA-BAPB was similar to that of PMDA-ODA. According to Pater *et al.*⁷, combined crazing and shear yielding occur in semicrystalline polyimides. They showed that many crazes with yielding are observed when crystallinity is low and few crazes are observed when crystallinity is high. They suggested that crystal acts like cross-links or entanglements and BPDA-PDA shows only shear yielding because it has a probability to be crystallized. Therefore it is supposed that in this study local molecular order might act like crystal in semicrystalline polyimides, although local molecular order is not real crystal. Qualitatively, it is difficult for craze to grow in BPDA-PDA, PMDA-ODA and PMDA-BAPB due to a high degree of local molecular order and low chain mobility. So, deformation only occurred via shear yielding, while PMDA-BAPP with a low degree of local molecular order and high chain mobility, which had a probability to be fibrillated, showed combined crazing and shear yielding. These phenomena are summarized in Table 4.

CONCLUSIONS

The deformation and fracture behaviour of thin polyimide films in single edge notched tension and tear test was investigated and the results were correlated with the degree of local molecular order measured by packing coefficient.

It was found that the tear energy showed maximum value as packing coefficient increased. Above critical

Table 3 Yield stress of polyimide films as a function of imidization temperature in tensile test

Polyimide	Imidization temperature (°C)				
	200	250	300	350	400
BPDA-PDA	175 ± 5	181 ± 10	237 ± 17	220 ± 17	214 ± 18
PMDA-ODA	99 ± 6	95 ± 4	96 ± 4	101 ± 11	120 ± 8
PMDA-BAPB			Fracture occurred before yielding		
PMDA-BAPP	89 ± 4	72 ± 15	88 ± 3		

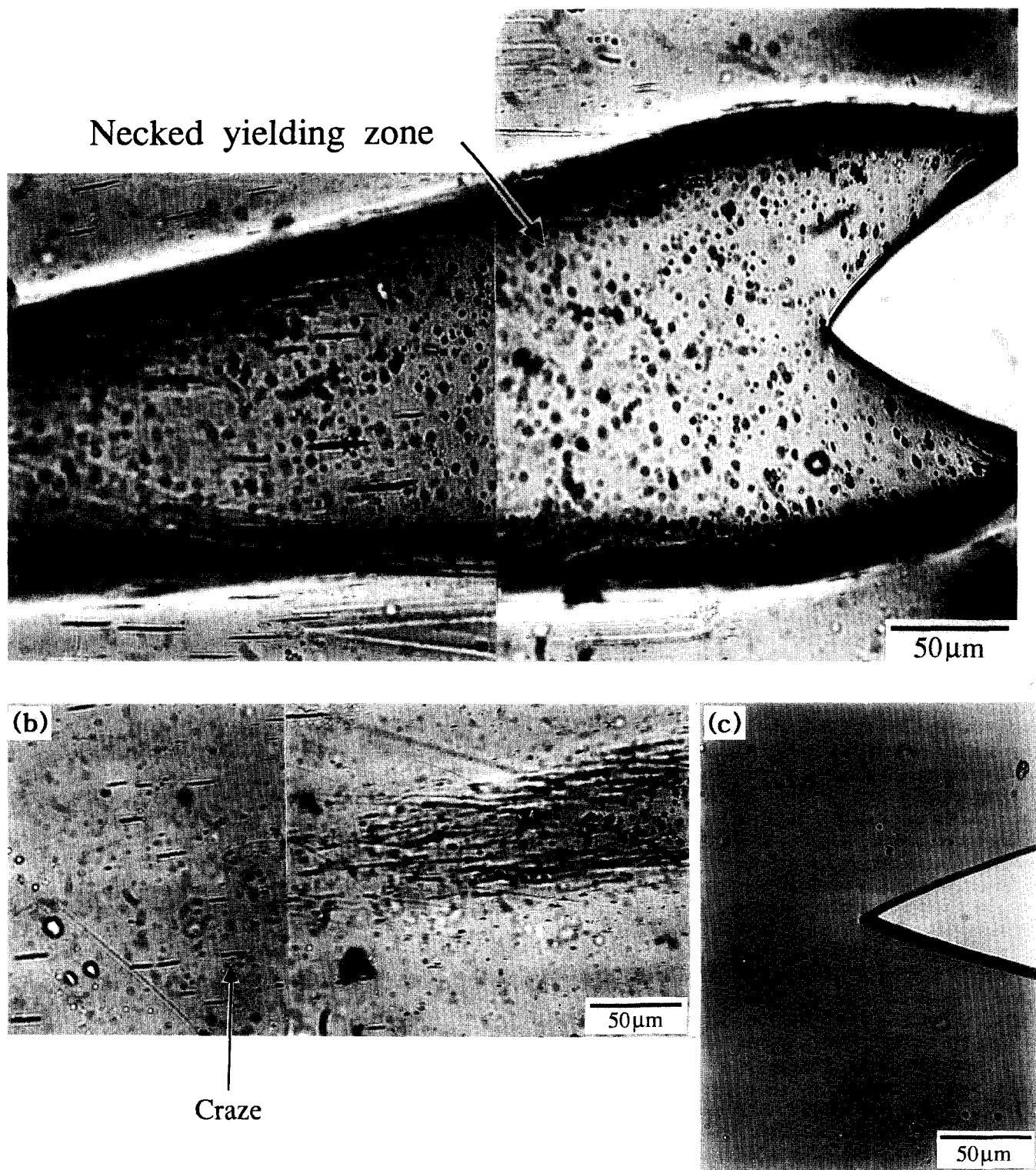


Figure 12 Crack tip region of polyimide films in single edge notch tension: (a) PMDA-BAPP at the crack tip, (b) PMDA-BAPP at distant region from the crack tip, (c) PMDA-ODA

Table 4 The deformation mechanism and packing coefficient

Polyimide	Packing coefficient	Deformation mechanism
BPDA-PDA	0.706–0.726	Shear yielding
PMDA-ODA	0.687–0.691	Shear yielding
PMDA-BAPP	0.698–0.704	Shear yielding
PMDA-BAPP	0.683–0.685	Shear yielding and crazing
LARC-TPI ^a	0.673	Shear yielding and crazing

^a From ref. 8

packing coefficient, the films became so brittle that the tear energy decreased. Also the tear energy increased as the flexibility of polyimide backbone increased. Fracture behaviour of polyimide films cured at low temperature was different at both sides of the film, substrate-side and air-side, whereas this heterogeneous fracture behaviour disappeared in films cured at high temperature. These results might be attributed that the local molecular order

was formed in the film near the surface of substrate at low curing temperature and it advanced in the direction of the opposite side as curing temperature increased. PMDA-BAPP with low degree of local molecular order and high chain mobility was deformed by crazing with shear yielding. Other polyimides with high degree of local molecular order and high chain mobility showed only shear yielding.

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