Essential and Non-essential Work of Fracture of PI/SiO₂ Hybrid Thin Films

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Received: 6 July 2006 / Accepted: 8 November 2006 /

Published online: 4 January 2007

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Abstract Essential work of fracture (EWF) analysis is used to study the effect of the silica doping level on fracture toughness of polyimide/silica (PI/SiO₂) hybrid films. By using double-edge-notched-tension (DENT) specimens with different ligament lengths, it seems that the introduction of silica additive can improve the specific essential work of fracture (w_e) of PI thin films, but the specific non-essential work of fracture (βw_p) will decrease significantly as the silica doping level increasing from 1 to 5 wt.%, and even lower than that of neat PI. The failure process of the fracture is investigated with online scanning electron microscope (SEM) observation and the parameters of non-essential work of fracture, β and w_p , are calculated based on finite element (FE) method.

Key words thin film · fracture · plane-stress condition · EWF · SEM · FE method

1 Introduction

With the development of micro-electronics and micro-electro-mechanical systems (MEMS) in recent years, characterizing, understanding and controlling the mechanical and thermal properties of thin films have received great attentions [1–3]. As a class of important insulating material, PI thin films are receiving more attentions as working as buffer coatings, passivation layers, dielectrics and wafer scale packages because of the outstanding properties [4]. In order to further improving their properties, recent work has been focused on how to introduce some nano-structured inorganic additives into them since it is thought that the composite thin films might combine desirable organic and inorganic characteristics [5, 6].

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To satisfy the engineering application, the fracture toughness of PIs and their hybrid thin films will play a critical role. Although the linear elastic fracture mechanics (LEFM) approach is generally used to study the fracture occurring at the nominal stress well below the uniaxial yield stress of the material, it is redundant to use it to characterize the failure of PIs and their hybrid thin films since they are often regarded as a kind of ductile materials and a large plastic zone might be developed at the crack tip under loading.

As an alternative to LEFM, J -integral analysis has been successfully characterized the fracture behavior of the ductile materials, which was proposed by Rice [7] and is a path independent line integral expressed in terms of the energy as

$$J = - \frac{\delta U}{\delta a} \quad (1)$$

where U is the potential energy of the loaded body. Although the theoretical analysis [7] about J -integral has been well established and the experimental procedure has also been standardized [8], the testing standard requires that the specimen size along the crack front must meet the plane-strain condition determined by

$$B, W - a \geq 25 \left(\frac{J_c}{\sigma_y} \right) \quad (2)$$

where B and W are the specimen thickness and width, respectively, and σ_y is the uniaxial yielding stress of the material. According to Eq. 2, it is impossible to use J -integral method to assess the toughness characterization of polymeric thin films since the plane-stress condition instead of plane-strain condition is satisfied for the materials studied.

Another method for characterization of the fracture behavior of ductile materials is called essential work of fracture (EWF), originally proposed by Broberg [9]. Compared with the J -integral method, the requirement of the specimen size for EWF method is plane-stress conditions, and the more attractive is that one only needs to know the ligament length of specimens rather than measure the crack extension as requirement of the J -integral method. Therefore, much work has been carried out by using this method to evaluate the fracture behavior of ductile thin films [e.g. 10–12].

The aim of this work is to study the fracture toughness of PI/SiO₂ hybrid films by EWF method. The fracture process was analyzed by online SEM images, and the FE method was used to calculate the parameters of non-essential work of fracture, β and w_p , for specimens with different silica doping levels and different ligament lengths.

2 Theory of EWF Method

The EWF concept is initially developed by Cotterell and Reddel [13] on the basis of Broberg's idea [9], assuming that the non-elastic region at the tip of crack comprises two regions as depicted in Fig. 1: an inner fracture process zone (IFPZ), where fracture actually takes place; and an outer plastic deformation zone (OPDZ), where plastic deformation is necessary to accommodate the strain in the end region. The total work of fracture, W_f , is composed of the two above components:

$$W_f = W_e + W_p \quad (3)$$

Fig. 1 Schematic representations of **a** IFPZ and the OPDZ; **b** specific work of fracture of w_f versus ligament length (L)

where W_e termed ‘essential work of fracture’ is the work expended in the IFPZ to form a neck and its subsequent tearing. Physically, W_e is a surface energy term whose value is proportional to the ligament area (BL), i.e.

$$W_e = w_e BL \quad (4)$$

where B is the specimen thickness as defined before. L denotes the ligament length of specimens. w_e is called ‘specific essential work of fracture’ and considered to be a material constant for a given thickness.

W_p is the work dissipated in the OPDZ where various types of deformations such as shear yielding and micro-voiding might be existed. This work is termed ‘non-essential work of fracture,’ whose value is proportional to the volume of the yielded zone (BL^2), i.e.

$$W_p = \beta w_p BL^2 \quad (5)$$

where w_p is called ‘specific non-essential work of fracture per unit volume.’ β is the plastic zone shape factor, whose value depends on the geometry of the specimen and the crack.

Introducing Eqs. 4 and 5 into Eq. 3 gives:

$$w_f = \frac{W_f}{BL} = w_e + \beta w_p L \quad (6)$$

where w_f is termed ‘specific total work of fracture.’

According to Eq. 6, the plot of w_f as a function of L should be a linear relation, whose interception with Y-axis and the slope are w_e and βw_p , respectively. Thus, the EWF method consists of testing specimens with different ligament lengths, registering w_f for each (area under the force-displacement curve), plotting w_f versus L curves and calculating the best-fit regression line.

Physically, w_e is the work required to create two new fracture surfaces and is consumed in the fracture processes involved. For the fracture mode of I type, it can be defined theoretically as the following

$$w_e = J_c = d \int_0^{\bar{\varepsilon}_n} \bar{\sigma} d\bar{\varepsilon} + \int_{d\varepsilon_n}^{\delta_{1c}} \sigma(\delta) d\delta \quad (7)$$

where d is the fracture process zone width and is of the order of the sheet thickness. $(\bar{\sigma}, \bar{\epsilon})$ are the true stress/strain. $\bar{\epsilon}$ and ϵ_n are the true and engineering necking strain. σ and δ are the stress and crack tip opening displacement within the fracture process zone. δ_{IC} is the mode I critical value of δ . The more detailed theoretical explanation about the relationship of EWF and J-integral methods can be referred [14].

In the EWF technique, it is common to employ the DENT specimen geometry (as shown in Fig. 1a). For determining the value of the plane-stress specific essential work of fracture for polymer films, the DENT geometry was employed by the ESIS protocol [15], and the following conditions were suggested:

- a) In order for the valid measurement of w_e , the ligament L has to satisfy the following requirement

$$3 - 5B \leq L \leq \min\left(\frac{W}{3}, 2r_p\right) \quad (8)$$

where r_p is the radius of the plastic zone at the crack tip.

About the Eq. 8, $L \leq 2r_p$ is to ensure that complete yielding of the ligament region occurs prior to crack growth, hence maintaining the proportionality of W_p and L^2 ; $L \leq W/3$ is to ensure that the size of the plastic zone is not disturbed by the edge effect and the plastic deformation is confined to the ligament area; $L \geq 3-5B$ is to ensure that the state of stress in the ligament region is one of pure plane-stress and not mixed modes (as shown in Fig. 1b).

- b) In order for a ductile DENT specimen to fail in a ductile manner, the proper alignment of the two edge cracks is very important. It has been pointed out that if the paths of the propagating crack from notch tips are not fully co-linear, premature failure will occur [15].

3 Preparation of Specimens

In order to produce PI/SiO₂ nanocomposite films, a new sol–gel technique was employed in this study. The traditional PI/SiO₂ hybrid films by sol–gel technique possess lower coefficient of thermal expansion (CTE), higher thermal stability and better mechanical properties at room temperature compared with neat PI films. However, the mechanical properties of PI/SiO₂ hybrid films by the traditional process will decrease fast by the addition of SiO₂ particles at higher silica content because of the fast increase of particle size. In order to improve the properties of PI/SiO₂ hybrid films, a new process, which would lead to a smaller particle size than the traditional process, was developed for the preparation of PI/SiO₂ hybrid films in this study. The new synthesis process mainly includes two steps of reactions: hydrolysis of alkoxides to produce hydroxyl groups, followed by the polycondensation of the hydroxyl groups and residual alkoxides groups to form a three-dimensional network. The detailed introduction about the synthesis of PI/SiO₂ hybrid films and the related tensile properties can be found in the literature [16]. Four different types of films were finally prepared for EWF experiments according to the difference of silica doping levels: 0 wt.%, 1 wt.%, 3 wt.%, and 5 wt.%.

For EWF test, both double-edge-notched-tension (DENT) and single-edge-notched-tension (SENT) specimen geometries were ever used. However, it seems that DENT is more convincing because the symmetric specimen geometry can ensure a simple stress state existed in the ligament zone. Therefore, DENT specimens with width (W) of 30 mm and overall

Fig. 2 Typical load-displacement for DENT specimens with different ligament lengths

length (H) of 110 mm were used for EWF experiment in this study. The specimens were prepared by first cutting the sheets into rectangular coupons ($W=30$ mm, $H=110$ mm). The longitudinal axis of the coupons was perpendicular to the long edge of the sheet. Coupons were then razor notched to produce DENT specimens with a series of ligament length (L) values: 5, 8, 12, 16 and 20 mm, respectively. To ensure that two notches were aligned, a line was drawn across the width of the specimen at its mid-point prior to notching.

After preparation, each specimen was tested to complete failure with a Sans universal table-testing machine using special clamps for films with initial separation (Z) of 70 mm. The testing was performed at a crosshead displacement rate of 0.2 mm/min. The load-displacement (P - δ) curves were recorded using a compute data logger.

4 Experimental Results and Calculation

4.1 Specific Essential Work of Fracture

The EWF tests on DENT type specimens produced load-displacement curves were received. Figure 2 shows the result of PI/SiO₂ hybrid films with 1 wt.% silica doping levels, and the similar result can be found for other specimens. According to Fig. 2, it seems that the variation in ligament length has no great influence on the general behavior of the load-displacement curves. The notable feature of these curves is their geometrical similarity, which is the basic requirement for determining w_e . Maximum load, extension to break and the total area under the curve will increase with increasing the ligament length.

Fig. 3 Load versus deflection curves of three typical fracture modes (a: brittle fracture, b: unstable ductile fracture, c: stable ductile fracture)

In order to give a comparison, Fig. 3 shows the typical fracture modes of materials (Fig. 3a, b and c corresponding to brittle fracture, unstable ductile fracture and stable ductile fracture, respectively). Compared Fig. 2 with Fig. 3, it can be found that the fracture mode in this study is partly similar with Fig. 3b and c. Therefore, the failure mode in this study belongs to a kind of ductile fracture, but does not realize stable crack development. The possible reason is that it is very difficult to accurately pre-cut two symmetric edge cracks which have the same length and are fully co-linear to avoid premature failure.

The SEM images are shown in Fig. 4. Among all of them, Fig. 4a corresponds to the initial state that no force is applied. By magnifying it as shown in Fig. 4b, it can be found that the pre-cut edge crack does not meet the requirement of sharp crack and there exists the irregular deformation ahead of the crack tip. With the crack having a little development, the crack tip (Fig. 4c and d) becomes more sharp than the free state. Since it is very difficult to accurately pre-cut two symmetric sharp edge cracks, the crack development is an unstable process. One crack front advances a little quicker than the other at first, then becomes a dominate factor that leads to the final failure of the specimen, as shown in Fig. 4e and f. Therefore, it is difficult to receive a stable failure process, which might affect the determination of w_e and lead to the experimental value to be a little lower than the real value.

Figure 5 shows the result of the specific work of fracture, w_f , versus ligament length L for PI/SiO₂ hybrid films with different silica doping levels. It can be seen that for the range of ligament lengths studied here, the variation of w_f with L is basically linear and the silica doping level has a significant effect on w_f testing results. Compared with neat PI thin films, w_f has a great increase for hybrid films with 1 wt. % silica doping level. However, with further increase of silica content, w_f will decrease in reverse.

Based on the EWF theory, the fracture tough of thin films can be assessed by the specific essential work of fracture, w_e , which can be received by linear interpolation with Y-axis in Fig. 5. The result was shown in Fig. 6. Compared with that of neat PI, w_e of hybrid thin films with 1 wt. % silica doping level increases about 12%, then has a little decrease but still higher than that of neat PI as further increase of silica content. Although it has

Fig. 4 SEM images on the crack developing with increasing of the applied load

demonstrated that coefficient of thermal expansion (CTE) can be greatly decreased by introducing more silica (as higher as 8 wt.%) into PI matrix [16], the result in Fig. 6 demonstrates that it is not effective to improve the fracture toughness by introducing more silica additive. The possible reason is that silica belongs to a kind of fragile materials. The existence of low quantity of nano-silica particles might play as an obstacle for the initiation of the crack, but too much silica content will decrease the toughness of composite films in reverse.

4.2 Specific Non-essential Work of Fracture

As stated above, the total energy expanded in EWF experiment can be divided into two parts, the fracture work for forming new surfaces and the plastic work for forming yielding

Fig. 5 Specific work of fracture (W_f) versus ligament length (L) affected by silica doping levels

Fig. 6 Essential work of fracture as a function of silica doping levels

Fig. 7 Non-essential work of fracture as a function of silica doping levels

deformation along the ligament zone, which is called specific non-essential work of fracture and denotes as βw_p . According to Eq. 6, βw_p corresponds to the slope of the specific work of fracture, w_f , versus the ligament length, L . Therefore, based on the experimental result in Fig. 5, the result of βw_p as a function of silica doping levels can be calculated and shown in Fig. 7. Compared with the specific essential work of fracture, the specific non-essential work of fracture of PI/SiO₂ hybrid thin films has a significant decrease with silica doping level increasing from 1 wt.% to 5 wt.%. Since βw_p reflects the plastic deformation capability of specimens along the ligament direction and w_e denotes the required energy to form new surface, as stated above that silica belongs to a kind of fragile materials, it is understandable that βw_p will decrease more quickly than w_e as more silica additive is introduced.

The specific non-essential work of fracture, βw_p , includes two parameters, the specific plastic work of fracture per unit volume (w_p), and the shape factors (β), which is defined as

$$\beta = h/L \quad (9)$$

where h is the real height if a diamond plastic zone was assumed. Otherwise, h denotes an equivalent height of the plastic zone.

Although it is more reasonable to treat the plastic work based on the whole specific plastic energy, βw_p , the determination of β has other interesting aspects as analyzing the shape of the plastic zone for different ductile thin films in EWF experiment. Traditionally, the determination of β was based on visual or optical microscopic observation of the diffused stress-whitened zone along the ligament during EWF experiment and then some ideal plastic shapes (e.g. circle, diamond and elliptical) were assumed [17]. In fact, it is very

Fig. 8 Evolution of plastic zone for neat PI thin films ($L=8$ mm)

difficult to accurately measure the shape of the plastic zone by visual or optical microscopic observation in EWF experiment. In order to give β -value more convincingly, the finite element calculation is used in this study. As stated above, the volume of the plastic zone under maximum loading for DENT experiment is defined as βBL^2 , therefore, the plastic zone shape factor, β , can be received by calculating the real volume of the plastic zone by FE method divided by BL^2 . The related material's constants needed for FEM calculation, e.g. Young's modulus, Poisson ratio, yielding strength, have been received by the uniaxial tensile specimens without pre-cracks.

Figure 8 shows the evolution of the plastic zone with increase of loading. Since the structure of specimens is symmetric, only half of the specimen is calculated, and the plastic zone was shown as red in Fig. 8 (P and $P_{\max}$ denote the applied load and the maximum load of EWF experiment, respectively). It is clear that the plastic zone starts from the tip of the

Fig. 9 Comparison of the stress along loading direction (Fig. a, b and c) and Von mises stress (Fig. d, e and f) for hybrid thin film with 1 wt.%SiO₂ under $P_{\max}$

Fig. 10 Shape factor versus ligament length for specimens with different silica doping levels

crack, then develops as a ring. With further increase of the load as shown in Fig. 8c and d, the yielding ring will develop into a solid area.

The comparison of the stress along loading direction and Von mises stress of hybrid thin films with 1 wt. % silica doping level for $L=5$, 12 and 20 mm is shown in Fig. 9. Different from the commonly assumed, the final plastic zone for $L=20$ mm is not a solid area, but a

Fig. 11 w_p versus L for specimens with different silica doping levels

ring. Moreover, although the linear relationship of w_f versus L is still satisfied for $L=20$ mm as shown in Fig. 5, the significant difference between the stress along the loading direction and Von mises stress demonstrates that a complicated stress state is existed, which is caused by the effect of free edge. Therefore, although much work has demonstrated that the request of $L \leq W/3$ does not need to strictly satisfy for determining the specific essential work of fracture in EWF experiment, it seems that too larger ligament might affect the testing result of specific non-essential work of fracture.

According to the above calculating result, Fig. 10 shows the β -values under different silica doping levels and ligament lengths. As β has been received, w_p can be easily calculated and the result is shown in Fig. 11. It is clear that the w_p for hybrid thin films with 5 wt. % Silica doping level is significantly lower than other testing result, which also demonstrates that too higher silica doping level will decrease the plastic deformation capability of hybrid thin films.

5 Conclusions

The EWF method has been used to characterize the fracture properties of PI/SiO₂ hybrid thin films by DENT specimens. The load-displacement curves at various ligament lengths and different silica doping levels show a great geometrically similar to one another. A linear relationship is existed between the total specific work of fracture, w_f , and ligament length, L for four types of specimens studied here. It seems that the values of w_f , w_e and βw_p will be improved by introducing inorganic nano-silica additive into PI substrate and the maximum value corresponds to the hybrid thin film with 1 wt.% silica content. With further increase of silica content, w_e will have a little decrease, but is still higher than neat PI film. However, βw_p decreases monotonously and quickly as silica content increasing from 1 wt.% to 5 wt.%, and is even lower than that of neat PI film. The possible reason might be the reduced capability of plastic deformation of composite films with too higher fragile inorganic additive included.

By finite element calculation, the evolution process and the final shape of the plastic zone for EWF specimens was received. Different from the traditional assumed that the plastic zone should be a solid area, the calculating result demonstrates that a plastic ring is initiated at first, then maybe develops into a solid area, maybe not. The calculating result also demonstrates that a complicated stress state will be existed as with larger ligament length.

Acknowledgements This work was funded by Natural Science Foundation of China (No 10502005).

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