THE MECHANICS OF INTERFACE FRACTURE IN LAYERED COMPOSITE MATERIALS: (7) ADHESION TOUGHNESS OF MULTILAYER GRAPHENE MEMBRANES – NANOSCALE INTERFACE FRACTURES

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ABSTRACT

Adhesion toughness between graphene membranes and substrate is mode mixity dependent. Various experimental and analytical methods are discussed on the calculation of the adhesion toughness. The presence of sliding in multilayer graphene membranes increases the fracture mode mixity G_I/G_{II}, leading to a decrease in adhesion toughness measurements when using the circular blister test under either pressure load or point load. Once the mode I and II adhesion toughness are known, the adhesion toughness under general service loading conditions can be determined by using mixed mode partitions based on 2D elasticity and a linear failure criterion. The adhesion energy defined in literatures is generally different from the adhesion toughness unless the mode I adhesion toughness is equal to mode II adhesion toughness.

1 INTRODUCTION

Graphene membrane and insulating SiO_2 substrate composite materials are the most commonly used electronic device configurations. The adhesion toughness between the graphene membranes and SiO_2 substrates has attracted attentions of many researchers in recent years. Various experimental and calculation methods have been reported in literature to determine the toughness with various outcomes. It is well known that adhesion toughness or interface fracture toughness is mode mixity dependent with smallest value at mode I fracture and the largest value at mode II fracture. Many previous studies show that the toughness varies linearly between these two extremes for interfaces of low fracture toughness in both macroscopic interface fractures [1, 2] and microscopic interface fractures [3, 4]. The low adhesion toughness between graphene membranes and SiO_2 substrates is well into this category of low fracture toughness. However, as far as the authors' knowledge is concerned, the work [5] is the only study so far takes the mode mixity into consideration. In addition, the work [5] also firstly considers the effect of sliding on the mode mixity between multilayer graphene membranes. Moreover, it is worth noting that adhesion energies defined in some existing literature are different from adhesion toughness. The present work aims to report several experimental and analytical methods to determine the adhesion toughness between multilayer graphene membranes and substrates. Some previous confusions are understood.

2 EXPERIMENTAL AND ANALYTICAL METHODS

2.1 Double cantilever beam test (DCB)

Fig. 1 shows a schematic of the DCB specimen for the measurement of the adhesion toughness between a monolayer graphene and copper by DCB fracture mechanics testing [6]. The layups and loading conditions are also shown. For the test, both Si beams are loaded and unloaded at a constant displacement rate while the applied load is monitored as a function of the displacement. Multiple loading/crack growth/unloading cycles were performed to measure the crack lengths and the adhesion toughness of the as-grown graphene on copper. The measured crack length a and load P are also shown for each cycle.

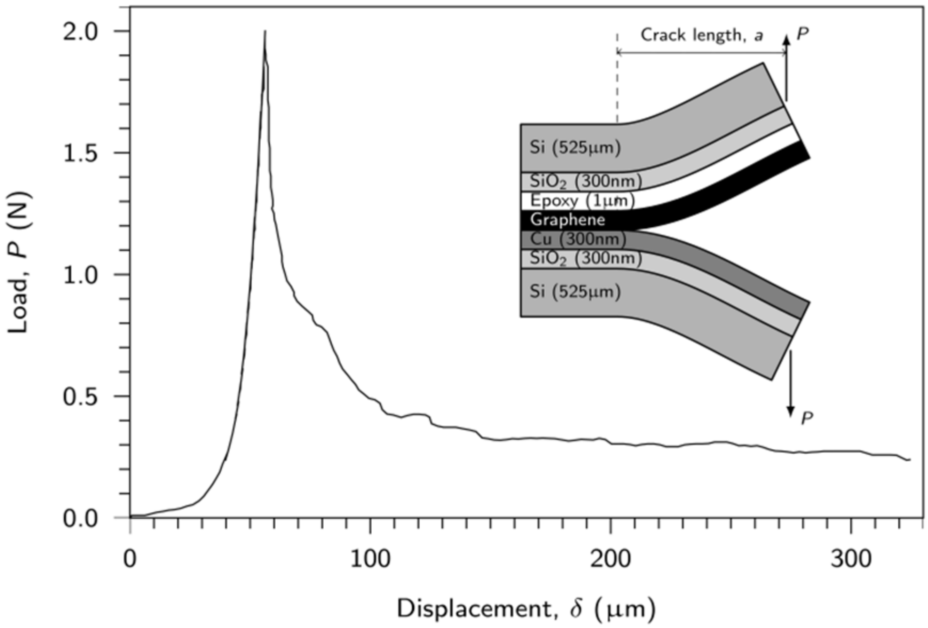

Figure 1: Measurement of the adhesion toughness between a monolayer graphene and Copper by DCB fracture mechanics testing (Copy from ref. [6]).

It is seen from Fig.1 that the DCB can be regarded as a symmetric DCB on pure mode I loading since the thickness of Si is much larger than the thickness of other materials. Moreover, since the thickness of Si, i.e. $h = 525\,\mu\text{m}$ is of macroscopic size. The interface fracture toughness is given by the classical partition theory [1, 2] and easily calculated by

$$G_c = G_{Ic} = \frac{12P_c^2 a^2}{Eb^2h^3} \tag{1}$$

where E is the Young's modulus of Si, a is the crack length shown in Fig. 1 and b is the width of the DCB. The authors are unable to find the values of both E and b used in the work [6]. The study [6] used the following equation to calculate the adhesion toughness.

$$G_c = \frac{12P_c^2 a^2}{Eb^2h^3}\left(1 + 0.64\frac{h}{a}\right)^2 \tag{2}$$

Measurements [6] of adhesion toughness are shown in Table 1 by using the data in Fig. 1 and Eq (1) and (2) where $\overline{G}_c$ is defined as

$$\overline{G}_c = \frac{Eb^2h^3}{12}G_c \tag{3}$$

It is seen that both Eq (1) and (2) give close predictions. The averaged $\overline{G}_c$ are 35.33 N^2mm^2 and 37.37 N^2mm^2 from Eqs. (1) and (2), respectively. The study [6] states that G_c has the value of $0.72 \pm 0.07\,\mathrm{J/m^2}$. Therefore, Eq. (1) gives $G_c = G_{Ic} = 0.68\,\mathrm{J/m^2}$ which is the critical mode I ERR or mode I fracture toughness. The present authors have no knowledge of the value of G_{IIc} which is usually much larger than G_{Ic}. When both G_{Ic} and G_{IIc} are known the fracture toughness under general loading conditions can be obtained by using ERR partition theories and failure criteria. The work [6] called the adhesion toughness as adhesion energy.

$a\,[\mathrm{mm}]$	$P_c\,[\mathrm{N}]$	$\overline{G}_c\,[\mathrm{N^2mm^2}]$, Eq. (1)	$\overline{G}_c\,[\mathrm{N^2mm^2}]$, Eq. (2)
5.5	1.1	36.60	41.21
8.6	0.748	41.38	44.68
11.1	0.528	34.35	36.46
13.32	0.418	31.00	32.58
16.06	0.352	31.96	33.31
18.74	0.308	33.32	34.52
21.18	0.286	36.69	37.87
23.11	0.264	37.22	38.31
Average values		35.33	37.37

Table 1: Measurements of adhesion toughness between monolayer graphene and copper using DCB [6].

The study [7] also used the name of adhesion energy concept and developed a very different method to calculate it. In the study [7] the adhesion energy is defined as

$$U_{\mathrm{total}} = U_{vdw} + U_e \tag{4}$$

where the van der Waals interaction energy U_{vdw} is calculated by using Lennard-Jones potential and U_e is the residual in-plane strain energy in the monolayer graphene due to interface mismatch and surface effect. The study gives $U_{vdw} = 0.16\,\mathrm{J/m^2}$, $U_e = 0.58\,\mathrm{J/m^2}$ and $U_{\mathrm{total}} = 0.74\,\mathrm{J/m^2}$. It is interesting to note that U_{total} is very close to either $G_c = G_{Ic} = 0.68\,\mathrm{J/m^2}$ from Eq. (1) or $G_c = 0.72 \pm 0.07\,\mathrm{J/m^2}$ from Eq. (2). But the physical meaning of Eq. (4) is completely different from that of Eqs. (1) and (2). More discussions on Eq. (4) will be given later.

Again, the study [8] also used the name of adhesion energy and used atomic force microscopy (AFM) to measure it. By using the Maugis-Dugdale equation

$$W_{\mathrm{adh}} = \frac{F_{\mathrm{adh}}}{1.77\pi R_{\mathrm{tip}}} \tag{5}$$

The adhesion energy W_{adh} is determined to be $0.11\,\mathrm{J/m^2}$ where F_{adh} is the pull-off adhesion force and R_{tip} is the radius of the microsphere tip. Obviously, this value is far from either $G_c = G_{Ic} = 0.68\,\mathrm{J/m^2}$ from Eq. (1) or $G_c = 0.72 \pm 0.07\,\mathrm{J/m^2}$ from Eq. (2). To improve the measurement the study [8] used the modified Rumpf model which takes the roughness of the microsphere tip into consideration and gave $W_{adh} = 0.75\,\mathrm{J/m^2}$. Obviously, this is very close to either $G_c = G_{Ic} = 0.68\,\mathrm{J/m^2}$ from Eq. (1) or $G_c = 0.72 \pm 0.07\,\mathrm{J/m^2}$ from Eq. (2). Again, the method in [8] is completely different from Eqs. (1), (2) and (4). It is interesting to note that Eq. (5) gives $W_{\mathrm{adh}} = 0.11\,\mathrm{J/m^2}$ close to $U_{vdw} = 0.16\,\mathrm{J/m^2}$ in Eq. (4). The study [8] indicates that the roughness gives extra $0.64\,\mathrm{J/m^2}$ adhesion energy while the study [7] states that this is due to the residual in-plane strain energy $U_e = 0.58\,\mathrm{J/m^2}$. Since AFM measurement gives approximately the mode I adhesion toughness, the $W_{\mathrm{adh}} = 0.75\,\mathrm{J/m^2}$ is considered to be critical mode I ERR.

2.2 Circular blister test under pressure load

In general, the mode I ERR G_I and mode II ERR G_{II} for graphene membranes and thick substrate material systems can be written as [1-5]

$$G_I = c_I\left(M_B + M_{BR} - \frac{N_B + N_{BR}}{\beta_{2-2D}} - \frac{P_B}{\beta_{3-2D}}\right)^2 \tag{6}$$

$$G_{II} = c_{II}\left(M_B + M_{BR} - \frac{N_B + N_{BR}}{\theta_{2-2D}}\right)^2 \tag{7}$$

Since the thickness of graphene membranes is in nanoscale Eqs. (6) and (7) are based on 2D elasticity partitions as indicated by the subscript 2D. The crack tip bending moment per unit width M_B and in-plane axial force per unit width N_B are the externally applied parts while the M_{BR} and N_{BR} are the residual parts due to residual stresses. P_B is the crack tip through thickness shear force per unit width. In the case of zero residual bending moment and axial force, the work [5, 9, 10] gives the mode mixity ratio $\rho = G_I/G_{II}$ as

$$\rho = \frac{1}{0.6059}\left(\frac{0.7578 - 0.1429\nu + \lambda}{1.400 + 0.2358\nu}\right)^2 \tag{8}$$

The total ERR G is given as

$$G = G_J + G_S = G_J(1+\eta) \tag{9}$$

Jensen's G_J component can be calculated as [9, 10]

$$G_J = \vartheta(\upsilon)p\delta \tag{10}$$

The ratio $\eta = G_S/G_J$ is

$$\eta = \frac{\lambda(\lambda + 1.516 - 0.2858\nu)}{1.761 + 0.1835\nu + 0.05413\nu^2} \tag{11}$$

p and δ in Eq. (10) represent the pressure load and the center deflection of the blister, respectively. The λ parameter in Eqs. (8) and (11) represents the effect of sliding in multilayer graphene membranes and $\vartheta(\nu)$ is a Poison's ratio ν -dependent parameter, details of which can be found in the work [5].

The study [11] reported adhesion toughness between multilayer graphene membranes and SiO_2 substrates using circular blister tests under pressure load. The adhesion toughness was calculated using Eq. (10) [11]. For monolayer graphene membrane the toughness was found to be $G_c = 0.45 \pm 0.02\,\mathrm{J/m^2}$ while for multilayer graphene membranes it was $G_c = 0.31 \pm 0.03\,\mathrm{J/m^2}$.

By using Eqs. (8) to (11) in the present work, it is found that the presence of sliding in multilayer graphene membranes increases the fracture mode ratio G_I/G_{II}, leading to a decrease in adhesion toughness measurements when using the circular blister test. The mode mixity jumps up from 43% for the monolayer graphene membranes to about 77% for multilayer graphene membranes. This increase in the mode mixity has the effect of lowering the adhesion toughness G_c from $0.424\,\mathrm{J/m^2}$ to $0.365\,\mathrm{J/m^2}$. The critical mode I and mode II adhesion toughness are determined to be $G_{Ic} = 0.230\,\mathrm{J/m^2}$ and $G_{IIc} = 0.666\,\mathrm{J/m^2}$, respectively.

Using Eq. (4) the study [7] gives $U_{vdw} = 0.266\,\mathrm{J/m^2}$, $U_e = 0.200\,\mathrm{J/m^2}$ and $U_{\mathrm{total}} = 0.466\,\mathrm{J/m^2}$ for monolayer. It is interesting to note that U_{total} is very close to either $G_c = 0.45\,\mathrm{J/m^2}$ in the work [11] or $G_c = 0.424\,\mathrm{J/m^2}$ in the present work. For multilayer graphene membranes, Eq. (4) in the study [7] gives $U_{vdw} \approx 0.272\,\mathrm{J/m^2}$, $U_e \approx 0.125\,\mathrm{J/m^2}$ and $U_{\mathrm{total}} \approx 297\,\mathrm{J/m^2}$. Again, it is interesting to note that U_{total} is very close to $G_c = 0.31 \pm 0.03\,\mathrm{J/m^2}$ in the work [11]. However, both the work [11] and the present work do not consider the residual strain energy. When the residual strain energy is considered, the residual axial force N_{BR} in Eqs. (6) and (7) needs to be included. But both the work [11] and the present work do not consider this residual force. Moreover, when the adhesion energy defined in Eq. (4) [7] is taken to be the adhesion toughness defined in Eq. (9) in present work and the study [11], the adhesion toughness is no longer dependent on mode mixity. That is, any combination of crack tip bending moment M_B, in-plane axial force N_B, through thickness shear force P_B, residual bending moment M_{BR} and residual axial force N_{BR} in Eqs. (6) and (7) will produce the same fracture toughness given by Eq. (4) [7]. This is only possible when the mode I adhesion toughness is equal to mode II adhesion toughness, i.e. $G_{Ic} = G_{IIc}$. However, this is generally not the case and G_{IIc} is much larger than G_{Ic}.

By using AFM and Maugis-Dugdale equation

$$W_{\mathrm{adh}} = \frac{F_{\mathrm{adh}}}{1.66\pi R_{\mathrm{tip}}} \tag{12}$$

The study [8] gives $W_{\mathrm{adh}} = 0.18\,\mathrm{J/m^2}$ for monolayer. By using the modified Rumpf model which takes the roughness of the microsphere tip into consideration, the study [8] gives $W_{\mathrm{adh}} = 0.46\,\mathrm{J/m^2}$ which is very close to $G_c = 0.45\,\mathrm{J/m^2}$ in the work [11] or $G_c = 0.424\,\mathrm{J/m^2}$ in the present work. Since AFM measurement gives approximately the mode I adhesion toughness, $W_{\mathrm{adh}} = 0.46\,\mathrm{J/m^2}$ is considered to be mode I toughness. However, it is much larger than the $G_{Ic} = 0.230\,\mathrm{J/m^2}$ in the present study. It is interesting to note that $W_{\mathrm{adh}} = 0.18\,\mathrm{J/m^2}$ [8] from Maugis-Dugdale equation is close to $G_{Ic} = 0.230\,\mathrm{J/m^2}$. To examine if $G_{Ic} = 0.230\,\mathrm{J/m^2}$ and $G_{IIc} = 0.666\,\mathrm{J/m^2}$ are the accurate values, the adhesion toughness of 5-layer graphene membrane blisters under point load is considered next.

2.3 Circular blister test under point load

The ERR partitions for circular blister under point load are very similar to Eqs. (6-11) [5]. By using $G_{Ic} = 0.230\,\mathrm{J/m^2}$, $G_{IIc} = 0.666\,\mathrm{J/m^2}$ and a linear failure criterion, the adhesion toughness between 5-layer graphene membranes and SiO_2 substrates is found to be $G_c = 0.438\,\mathrm{J/m^2}$. The experimental result [12] is $G_c = 0.437\,\mathrm{J/m^2}$. The agreement is excellent.

3 CONCLUSIONS

Adhesion toughness between graphene membranes and substrate is mode mixity-dependent. The sliding effect in multilayer membranes increases the mode I fracture mode energy release rate resulting in lower total adhesion toughness. Once the critical mode I and II adhesion toughness are determined the interface adhesion toughness under general service loading conditions can be found to guide practical designs. The experimental result from a point load blister test agrees excellently with the model prediction and therefore validates the present theoretical model. The adhesion energy defined in literatures is generally different from the adhesion toughness unless the mode I adhesion toughness is equal to mode II adhesion toughness.

REFERENCES

[1] C.M. Harvey and S. Wang, Experimental assessment of mixed-mode partition theories, *Composite Structures*, **94**, 2012, pp. 2057-2067 (doi: 10.1016/j.compstruct.2012.02.007).

[2] C.M. Harvey, M.R. Eplett and S. Wang, Experimental assessment of mixed-mode partition theories for generally laminated composite beams, *Composite Structures*, **124**, 2015, pp.10-18 (doi: 10.1016/j.compstruct.2014.12.064).

[3] S. Wang, C.M. Harvey and B. Wang, Room temperature spallation of α-aluminia films grown by oxidation, *Engineering Fracture Mechanics*, available online 14th March 2017 (doi: 10.1016/j.engfracmech.2017.03.002).

[4] C.M. Harvey, B. Wang and S. Wang, Spallation of thin films driven by pockets of energy concentration, *Theoretical and Applied Fracture Mechanics,* available on line 21st April 2017 2017 (doi: 10.1016/j.tafmec.2017.04.011).

[5] J.D. Wood, C.M. Harvey and S. Wang, Adhesion toughness of multilayer graphene membranes. (under review).

[6] T. Yoon et al, Direct measurement of adhesion energy of monolayer graphene as-grown on copper and its application to renewable transfer process, *Nano Lett.* **12,** 2012, pp.1448–1452 (doi: 10.1021/nl204123h).

[7] Y. He et al, Anomalous interface adhesion of graphene membranes, *Scientific Report*, **3**, 2013, pp. 1-7 (doi: 10.1038/srep02660).

[8] T. Jiang and Y. Zhu, Measuring graphene adhesion using atomic force microscopy with a microsphere tip, *Nanoscale* **7,** 2015, pp.10760-10766 (doi: 10.1039/c5nr02480c).

[9] H.M. Jensen, The blister test for interface toughness measurement, *Eng. Fract. Mech*. **40,** 1991, pp. 475–486 (doi: 10.1016/0013-7944(91)90144-P).

[10] H.M. Jensen, Analysis of mode mixity in blister tests, *Int. J. Fracture* **94,** 1998, pp.79–88 (doi:10.1023/A:1007555313162).

[11] S.P. Koenig, N.G. Boddeti, M.L.Dunn and J.S. Bunch, Ultra-strong adhesion of graphene membranes, *Nature Nanotechnology*, **6**, 2011, pp. 543-546 (doi: 10.1038/nnano.2011.123).

[12] Z. Zong, C.L. Chen, M.R. Dokmeci and K.T. Wan, Direct measurement of graphene adhesion on silicon surface by interaction of nanoparticles, *Journal of Applied Physics*, **107**, 2010, pp. 026104 (doi: 10.1062/1.3294960).