Measuring Elastic and Plastic Properties of PVK and CBP Thin Films using Triangular Pyramid Indenter

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Abstract: This paper describes an estimation of elastic and plastic properties of Poly (9-vinylcarbazole) (PVK) and 4,4'-Bis (N-carbazolyl)-1,1'-biphenyl (CBP) thin films by using a nano-indenter. PVK and CBP were coated in a thickness of 350-500 nm on a glass substrate for Organic Light Emitting Diode (OLED) devices by spin coating and vacuum deposition respectively. The measurement of Young’s modulus was carried out by the continuous indentation method. Plastic deformation properties were obtained by a method proposed by Higuchi et al. (2009) and Ogasawara et al. (2007), that is stress-strain curve is estimated in an equation of \( \sigma = R \varepsilon^n \). The results have shown that the elastic modules of PVK and CBP were 9.3 MPa and 9.5 MPa respectively, which are a little lower than those of Alq3 and \( \alpha \)-NPD reported in the previous paper. Further, the material constant \( n \) are 0.003 and 0.0007 for PVK and CBP respectively, which are much smaller than those of Alq3 and \( \alpha \)-NPD, suggesting that PVK and CBP have nearly elastic-perfect plastic properties. Therefore, it has been suggested that the reason why PVK and CBP thin films showed higher critical cracking strains more than 7% is resulted from the lower elastic modulus and the smaller work hardening rate \( (n) \) than those of Alq3 and \( \alpha \)-NPD whose critical cracking strains are 5.0% and 3.6% respectively.

Keywords: Nano indenter, Elastic modulus, Plastic deformation, Stress-strain relationship, Triangular pyramid indenter

1. Introduction
Organic semiconductors have emerged as a new class of materials that are being actively investigated worldwide, due to their practical implications in optoelectronic devices, solar cells, photo detectors, and field effect transistors, among others [1-3]. The electroluminescence of the organic semiconductors is a well-known phenomenon, which has become advantageous for practical applications in organic light emitting diodes (OLEDs). The recent successful demonstration of luminescent organic materials to exhibit high luminescent efficiency has projected OLEDs as viable alternatives for liquid crystal display (LCD), light bulb, and fluorescent lamp[4, 5]. Electroluminescent devices based on OLEDs demonstrate excellent characteristics, such as thin shape, self-luminosity, and high-speed operation [6]. In addition to the improved electroluminescent properties, these organic semiconductors offer the scope of ductility/flexibility, similar to many of the polymer materials. This opened up new exciting opportunities, demonstrating the prototyping of flexible display and lighting that could be fabricated by roll-to-roll processing on flexible substrates [7]. However, some of the authors have reported that even organic materials experience cracking at low strain as well as inorganic TCO [8]. Furthermore, for a typical OLED device, the crack initiation strain of each layer was evaluated, and a method for improving the ductility - in which the relatively less ductile layer is replaced by another more ductile material - was proposed [8]. In the meantime, understanding the mechanical properties of organic semiconductors seems to be an important aspect for realization of advanced flexible displays and lightings. In particular, during roll-to-roll processing, substantial tension is applied to the substrate to prevent wrinkling, and to keep it stable during fabrication. In addition, in the process of forming constitutional layers, the curls formed in the final product due to the temperature changes caused by heating and drying and the difference in thermal expansion of the constitutional materials is of serious concern. Therefore, designing a product and determining the production conditions without fracture or plastic deformation are highly warranted. This requires a comprehensive understanding of the elastic modulus, thermal expansion rate, and elastic and plastic deformation property of the constitutional materials. To the best of our knowledge, there are not many reports on the abovementioned mechanical properties of organic semiconductors [7, 9]. In the previous paper, the authors have analyzed the elastic and plastic deformation properties of organic luminescent
materials deposited on glass substrate by using nanoindentation techniques [10], so that the obtained data are applied to the design of flexible organic light emitting diodes (OLEDs) and production equipment using roll-to-roll process. In those cases, the technique was applied only to the small molecular type polymer thin films prepared by vacuum deposition. Herein, we have analyzed the elastic and plastic deformation properties of the large molecular type polymer thin films prepared by wet process, further the small molecular type polymer thin films which showed greater critical cracking strain were also investigated, in comparison to the previous results [8].

2. Experiment and Analysis Method

2.1 Test specimen and equipment

Poly(9-vinylcarbazole) (PVK) and 4, 4’- Bis (N-carbazolyl)-1, 1’-biphenyl (CBP) thin films were coated in a thickness of 345 nm and 500 nm on a glass substrate for organic light emitting diode (OLED) devices by spin coating and vacuum deposition respectively. CBP thin films was deposited by a multi chamber vacuum deposition system for OLED which equipped with cryogenic pumps to evacuate water vapor. CBP material was evaporated from aluminum nitride (AlN) crucibles heated by electric heaters with controlling the film thickness by a crystal thickness monitor at a deposition rate of 0.1-0.2 nm/s under a vacuum pressure less than 2 x 10-4 Pa. PVK thin films were coated in a wet process using a spin coater, then dried the solvent in an oven filled with the dry nitrogen. Nano-indentation test was performed using a Nano Indenter XP (produced by MTS Systems Corporation) attached Berkovich-type triangular pyramid indenter having a vertical angle of 115° at a load of less than 6 mN. In addition, to correct the effect of tip shape of the indenter, a correction curve was formed by measuring fused silica of known modulus.

2.2 Test methods and data analysis

2.2.1 Measuring the elastic modulus

Elastic modulus was measured by continuous stiffness indentation method [11]. The continuous stiffness measuring method is a method in which the indenter is minutely vibrated during the indentation test and the response to the vibration, the amplitude and the phase difference are acquired as a function of time, and in response to the continuous change of the depth, \( dP/dh \) is continuously calculated. The principle is shown in Fig.1, and typical load-penetration curve \((P-h)\) curve during loading and unloading is shown in Fig.2.

The total force (detected load component) \( F(t) \) in the direction in which the indenter enters the sample is expressed by the following equation.

\[
F(t) = m \frac{dh}{dt} + D \left( \frac{dh}{dt} \right) + Kh
\]

(1)

Here, the first term of Eq. (1) is the force derived from the indenter axis \((m: \text{mass of the indenter axis})\), the second term of Eq. (1) is from the viscous component of the sample and indenter system \((D: \text{Attenuation constant})\), the third term is the combined force \((K: \text{composite stiffness})\) derived from the compliance of the loading system \((load frame)\) and the leaf spring, the stiffness of the leaf spring supporting the indenter shaft, and \(t\) represents time. \(D\) and \(K\) in Eq. (1) are expressed by the following equations.

\[
K = \left[ \left( \frac{dh}{dp} \right) + C_i \right]^{-1} + K_i
\]

(2)

\[
D = D_i + D_e
\]

(3)

Here \(C_i\) is the compliance of the load frame, \(K_i\) is the stiffness of the leaf spring supporting the indenter axis, \(D_i\) is the attenuation constant of the indenter system, and \(D_e\) is the attenuation constant of the specimen. Also, since \(F(t)\) in Eq. (1) depends on time, it is expressed by the following equation.

\[
F(t) = F_0 \exp(i \omega t)
\]

(4)

Here, \(F_0\) is a constant and \(\omega\) is an angular frequency. Substituting Eq. (4) into Eq. (1) and substituting Eq. (5) which is a special solution of ordinary differential equations and solving the equation, \(dP/dh\) is calculated as in Eq. (6).

\[
h = h_0 \exp \{i(\omega t - \phi)\}
\]

(5)
Here, $\phi$ is a phase difference. In Eq. (6), $C_c$, $m$, and $K_s$ are known at the time of measurement, so by measuring the vibration amplitude ($h_0$), the phase difference ($\phi$) and the excitation vibration amplitude ($F_0$), by substituting the value calculated from Eq. (6) in response to continuous change in depth. Therefore, by substituting the value obtained by calculation into the Eq. (7) and assuming the Poisson’s ratio of the specimen, the reduced modulus is calculated based on the Sneddon flat punch solution [13], as determined by the following Eq. (8).

\[
\frac{dP}{dh} = \left( \frac{1}{(F_0 / h_0) \cos \phi - (K_s - m \phi^2)} + C_f \right)^{-1} \tag{6}
\]

Here, $a_e$ and $a_p$ are constants related to the elastic solution and rigid/perfect plastic solution, respectively [16].

(4) Representative strain $\varepsilon_r$, corresponding to the triangular pyramid indenter with a vertical angle of $\phi$ was determined by the following Eq. (11):

\[
\varepsilon_r = 0.157 \cot \theta \tag{11}
\]

where the constant value of 0.157 was determined by Ogasawara et al., considering the difference between conical indenter and the triangular pyramid indenter [16, 17].

(5) In general, polymers show some sort of deformation behavior. In this study, the relationship between stress and strain was assumed to follow a power law shown in Eq. (12), as a first step of the evaluation of thin polymer films for electronics device.

\[
\sigma = R \varepsilon^n \tag{12}
\]

Here, $R$ is a constant and $n$ is the strain hardening exponent. The value of $n$ was determined using a method proposed by Higuchi et al. The method is explained as follows.

In the proposed method by Ogasawara et al., in the case of a triangular pyramid indenter, since the representative strain of the analytical solution $\varepsilon_r$ does not depend on the indentation depth $h$, Stress-strain curve can be determined from experimental data which were obtained using plural triangular pyramid indenters having different tip angles [16]. On the other hand, Higuchi et al. has reported that in the experimental data, the relationship between the loading factor $C = P / h^2$ and $h$ of the load curve was a monotonically decreasing function, thus the representative stress $\sigma_r$, defined using the contact surface pressure, should be a monotonous decreasing [18]. Then, a monotonically decreasing function was set as $\zeta(h) = \beta / (1 + h)$, namely the relation of $\varepsilon_r = \beta / (1 + h)$, the stress-strain curve was estimated in the form of $\sigma = R \varepsilon^{(1+\delta) - 2}$ by using the appropriate constants. The authors also have reported that the loading factors $C = P / h^2$ for the organic materials Alq3, $\alpha$-NP and the inorganic material IZO were monotonically decreasing with respect to the penetration $h$, similar to the results of Higuchi et al.

In the present study, based on the same idea as Higuchi et al. [18], representative stress was set as a monotonically decreasing function $\varepsilon_r \propto \beta / h$, then the $n = (l_p - 2)$ was determined from the experimental data of $C = P / h^2$ by using the relation $C = P / h^2 = R h (\theta' - 2)$ since the stress strain curve is expressed as $\sigma = R \varepsilon^\theta = R h^\theta (\theta' - 2)$, finally the relation Eq. (12) of $\sigma = R \varepsilon^n$ was determined from $\sigma$ and $\varepsilon$. In other words, the work hardening index $n$ was calculated as being approximated by the reciprocal of the power $l_p-2$ of the indentation depth $h$ of the approximation formula of the loading factor $C = P / h^2$. 

\[
P = E \tan \theta
\]

\[
0.157 \cot \theta
\]

\[
R \varepsilon^n
\]
3. Results and Discussion

3.1 Load-penetration curve and elastic modulus

Figures 3 and 4 show the load-penetration depth diagram, elastic modulus- penetration depth diagram obtained for both CBP and PVK thin films. The elastic modulus- penetration depth diagrams were obtained only from the data of the region judged to have sufficiently secured the soundness and accuracy of the measurement system by verified using the standard sample for the measuring apparatus.

No remarkable difference among samples was found in the elastic modulus near the surface in both samples. However, when looking at the elastic modulus-penetration depth diagram shown in Fig.4, it is seen that the elastic modulus of PVK is higher than that of CBP at penetration depth of about 150 nm or more. In general, when the laminate material is measured by the nano-indentation method, the influence of the substrate is included in the measurement value as the indentation depth increases. Since the film thickness of PVK and CBP is 345 nm and 500 nm respectively, the influences of the substrate for PVK is greater than that of CBP. Therefore, in the calculation of elastic modulus, the range from 40 to 50 nm in the penetration depth was used, this is because, as can be seen from Fig. 4, in both cases, the elastic modulus increases when the indentation depth is 100 nm or more, and it is considered that the influence of the glass substrate is remarkably exhibited under these conditions. Therefore, in this study, as shown in Table 1, the elastic modulus in the region where the indentation depth is almost not affected by the glass substrate in the range of 40 nm to 50 nm was adopted as the measurement value of the elastic modulus of each thin film. Fig.5 shows a modulus of elasticity-penetration depth diagram obtained by measuring synthetic quartz which is a reference sample for the measuring apparatus. In the Fig.5, a smooth curve with less variation was obtained, and the result that the standard value $E = 74.8$ GPa was not greatly different was obtained over the entire measurement area where the indentation depth was about 40 nm or more. Therefore, it is judged that soundness and accuracy of the measuring device system are sufficiently secured in the main measurement. However, it should be noted that the error of $\pm 10\%$ was recognized in an indentation depth range from 40 to 50 nm used for measuring the elastic modulus.

Table 1 summarizes the reduced elastic modulus determined using the equations (6)-(8), and the representative strain and stress estimated using the equations (9)-(12). It was found that the CBP and PVK films had a reduced modulus ave.9.4 and ave.9.8 respectively. The obtained values were almost comparable or less to that of PET and PES, which are used in applications.

![Fig.3 Load vs penetration depth curves (P-h curve) of CBP and PVK thin films](image)

![Fig.4 Elastic modulus vs penetration depth curves of CBP and PVK thin films](image)

![Fig.5 Elasticity modulus-penetration depth diagram obtained by measuring synthetic quartz which is a reference sample](image)

<table>
<thead>
<tr>
<th>Table 1 Measured elastic modulus</th>
</tr>
</thead>
<tbody>
<tr>
<td>Young’s modulus [GPa]</td>
</tr>
<tr>
<td>CBP 5.5, 8.6, 8.4,</td>
</tr>
<tr>
<td>13.9, 7.9, 10.3,</td>
</tr>
<tr>
<td>6.8, 13.4,</td>
</tr>
<tr>
<td>PVK 9.0, 11.9, 9.2,</td>
</tr>
<tr>
<td>10.1, 8.8,</td>
</tr>
<tr>
<td>Ave.9.4, Ave.9.8,</td>
</tr>
<tr>
<td><em>(Standard deviation)</em></td>
</tr>
<tr>
<td><em>(Calculated by averaging the data of the penetration depth from 40 nm to 50 nm. Poisson's ratio of the sample was assumed 0.4.)</em></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 2 Summary of the reduced elastic moduli measured and the representative strain and stress estimated assuming to follow a power law the elastic modulus</th>
</tr>
</thead>
<tbody>
<tr>
<td>Materials Elastic modulus [GPa] Angle of triangular pyramid [deg] Included angle [deg] Elastic solution</td>
</tr>
<tr>
<td>---------------------------------</td>
</tr>
<tr>
<td>Al₃₄ 12.5 115 70.06 2/π tanθ 96.89 0.05696 21.9 226</td>
</tr>
<tr>
<td>α-NPD 13.5</td>
</tr>
<tr>
<td>CBP 9.4</td>
</tr>
<tr>
<td>PVK 9.8</td>
</tr>
</tbody>
</table>

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3.2 Estimation of stress-strain curve

The curves in Fig.2 consist of loading and unloading curves. The loading curve was used to estimate the stress strain curve. The loading curves corresponding to CBP and PVK are shown in Fig.6. The range of the penetration depth is less than 50nm. CBP film has greater deviation than PVK, suggesting non uniform mechanical property or surface roughness. In the optical microscopic observation of the surface as shown in Fig.7, fine droplets flying from the crucible called Splash are adhered during film formation using the vacuum evaporation method, but the density of the droplets is not much different from that of PVK, and overall the surface is smooth. In observation at high magnification using SEM as shown in Fig.8, a stripe-like irregularity perpendicular to the tensile direction and holes are observed on the surface of the CBP film although there is only a test piece with tensile strain of about 13% added, in comparison to that of PVK which is flat and no contrast. It is suggested that this striped unevenness is the result of the molecular arrangement and the degree of crystallization being different, that is, the inhomogeneity of the material is manifested by tensile strain.

Figure 7 illustrates the relationship between average contact pressure and penetration depth of CBP and PVK films. As mentioned earlier in section 2.2.1, the inverse of the obtained exponent is n for the Eq. (12). The corresponding n values were calculated to be 0.003 and 0.0007 in the cases of CBP and PVK, which are much smaller than those of Alq3 and α-NPD, as shown in Table 2, suggesting that PVK and CBP have nearly elastic-perfect-plastic properties. From these n, representative stress σr, representative strain εr, and the stress and strain curves were deduced, as shown in Table 2 and Figs.10. In the Fig.10, perfect elastic lines (σ = Erε) were also drawn using the obtained elastic modulus. In Fig.9, an approximate curve in the range of 5 nm to 50 nm from the surface was used for the above calculation, because firstly the region of several nm or less in the vicinity of the surface was excluded, since it is considered to have molecular specificity and surface specificity, secondly the surface roughness is not much different from that of PVK, and overall the surface is smooth as shown in Fig.7, thirdly the range of the penetration depth is less than 50nm. In Fig.10, an approximate curve in the range of 5 nm to 50 nm from the surface was used for the above calculation, because firstly the region of several nm or less in the vicinity of the surface was excluded, since it is considered to have molecular specificity and surface specificity, secondly data from 50 nm or deeper was also excluded to avoid the influence of glass substrate as mentioned above.

![Fig.7 Surface of the CBP thin film after applied a strain of 9% observed by an optical microscope](image1)

![Fig.8 Surface of the CBP thin film after applied a strain of 13% observed by an SEM](image2)

![Fig.9 Examples of relationship between average contact pressure and penetration depth of CBP and PVK](image3)

![Fig.10 Stress-strain curves deduced. (Curve of α-NPD is referred from ref. [13]](image4)
Some kinds of polymers may have viscoelastic property at elevated temperature or low strain rate, and hence the approach using simple power law might include a certain level of error. In micro mechanism, the formation of dislocation and enhancement of the dislocation density due to plastic deformation cause work hardening in metal. The other hand, in polymer materials where chain molecules are intertwined without crosslinking, the area intertwined, namely soft area, deforms with slipping at the beginning, then the chain molecules gradually deform into a structure with regularly oriented structure resulting in hardening [19]. In macro mechanism, at the early stage of the deformation in polymer materials, the relation of stress-strain is often expressed the power law equations [20], the relation can be used for the design and analysis in technological application. It has been suggested that strength and elastic modulus will be influenced by the strain rate according to many reports on the rate dependence of the strength and modulus of elasticity of polymer [21, 22]. Yamada et al. [23] have also suggested the strain rate dependency by the experiment using copper and the dynamic analysis considering the strain rate regarding the indentation test using the sharp tip indenter. However, the present study does not take into consideration the influence of the strain rate, which is a future task. Furthermore, in this research, we cannot deny the possibility that a crack is occurring at the time of loading because the electron microscope observation of the indentation has not been conducted.

The obtained data are summarized in comparison to the previous studies in Table 3. The critical cracking strains \( \epsilon_{cr} \) of CBP and PVK are higher than those of Alq3 and \( \alpha \)-NPD, meaning higher ductility. This could be explained their lower elastic modulus (\( E \)) and the lower strain hardening exponent (\( n \)) suggesting higher ductility. Since the crack was initiated at a strain range of 3–5% for Alq3, \( \alpha \)-NPD, mixed thin films of Alq3 and \( \alpha \)-NPD [8], it has been suggested that the thin films of organic luminescent materials prepared by physical vapor deposition caused cracking in the range of plastic deformation. This also implies that the obtained results would be useful to design flexible organic semiconductors with high flexibility, and to determine manufacturing conditions for roll-to-roll process without curl of the substrate, since the relation between curl and stress in the deposited films is shown in Eq. (13).

\[
\sigma_f = E_f \epsilon_f = \frac{E_t^2}{3(1-\nu)} R R_f
\]  

Where \( R \) is the radius of curl, \( \sigma_f, E_f, \epsilon_f \) and \( R_f \) are the generated stress, elastic modulus, strain and thickness of the films respectively, and \( E_t, t_f, \nu_f \) are the elastic modulus, thickness and Poisson’s ratio of the films respectively [24].

### Table 3 Summary of the obtained result

<table>
<thead>
<tr>
<th>Material</th>
<th>Type</th>
<th>Process</th>
<th>( r ) [( \text{Vacuum deposition} )]</th>
<th>( E_f [\text{GPa}] )</th>
<th>( n )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alq3</td>
<td>Small</td>
<td>Vacuum deposition</td>
<td><strong>5.0</strong></td>
<td><strong>35.6</strong></td>
<td><em><strong>0.658</strong></em></td>
</tr>
<tr>
<td>( \alpha )-NPD</td>
<td>Small</td>
<td>Vacuum deposition</td>
<td><strong>5.0</strong></td>
<td><strong>35.6</strong></td>
<td><em><strong>0.658</strong></em></td>
</tr>
<tr>
<td>CBP</td>
<td>Large</td>
<td>Spin coating</td>
<td><strong>7.3</strong></td>
<td><strong>9.5</strong></td>
<td><strong>0.003</strong></td>
</tr>
<tr>
<td>PVK</td>
<td>Large</td>
<td>Spin coating</td>
<td><strong>8.5</strong></td>
<td><strong>9.3</strong></td>
<td><strong>0.0007</strong></td>
</tr>
</tbody>
</table>

\*: Ref. [8], **: Ref. [23], ***: Ref. [10]

### 4. Conclusion

Reduced elastic moduli of organic luminescent materials deposited on glass substrate were measured by nanoindentation techniques. In addition, the relationship between stress and strain was discussed by assuming that the relationship follows a power law. Following are the conclusions derived from this study.

1. The reduced modulus of CBP and PVK were found to be around 9.4 and 9.8 GPa, which is slightly lower than those of Alq3 and \( \alpha \)-NPD.
2. The value of the exponent \( n \) in the power law (\( \sigma = R \epsilon^n \)) was estimated to be around 0.003 and 0.0007, corresponding to CBP and PVK thin films, which are much lower than those of Alq3 and \( \alpha \)-NPD.
3. It has been suggested that the reason why PVK and CBP thin films showed higher critical cracking strains more than 7% is resulted from the lower elastic modulus and the smaller work hardening rate (\( n \)) than those of Alq3 and \( \alpha \)-NPD whose critical cracking strains are 5.0% and 3.6% respectively.

As a further study, the effects of strain rate and cracking during loading on the elastic-plastic properties need to be investigated.

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