# CHAPTER V

# RESULTS AND DISCUSSION

This chapter provides the information about the results of polyimide and hyperbranch polyimide synthesis included the effects of varied layers polyether on the properties of the synthesized hyperbranch polyimide such as thermal properties, mechanical properties, dielectric properties and solubility.

## 5.1 Polyimide synthesis

### 5.1.1 Preparation of polyimide

All synthesized conditions and name definitions of synthesized polyimide are shown in Table 5.1. In this research, the polyimide are synthesized by a one-step reaction between 6 FDA, 3-4'ODA and DHBP (Dihydroxy diamino biphenyl) which have hydroxyl functional groups in a polyimide and end capped by PA (Phthalic Anhydride) in aprotic solvents to form polyamic acid (PAA), followed by the thermal imidization by azeotropic distillation of toluene for remove water from imide condensation polymerization. Because the hyperbranch reaction needed the soluble polymers, 6 FDA is chosen as a dianhydride to produce soluble polyimide. The content of hydroxyl function groups was controlled by changing the ratio of DHBP and ODA while keeping the ratio of dianhydride : diamine equal 1:1.

Table 5.1 Formulation and definition of polyimide

| Code | 6FDA mmol(g) | DHBP mmol(g) | ODA mmol (g) | PA mmol (g) |
|------|--------------|--------------|--------------|-------------|
| PI25 | 3.0000 (1.3326) | 0.7519 (0.1624) | 2.2558 (0.4512) | 0.0153 (0.0023) |
| PI50 | 3.0000 (1.3326) | 1.5039 (0.3248) | 1.5039 (0.3008) | 0.0154 (0.0023) |
| PI75 | 3.0000 (1.3326) | 2.2558 (0.4873) | 0.7519 (0.1504) | 0.0155 (0.0023) |
| PI100 | 3.0000 (1.3326) | 3.0078 (0.6497) | - | 0.0156 (0.0023) |

**6FDA**   **DHBP**   **ODA**
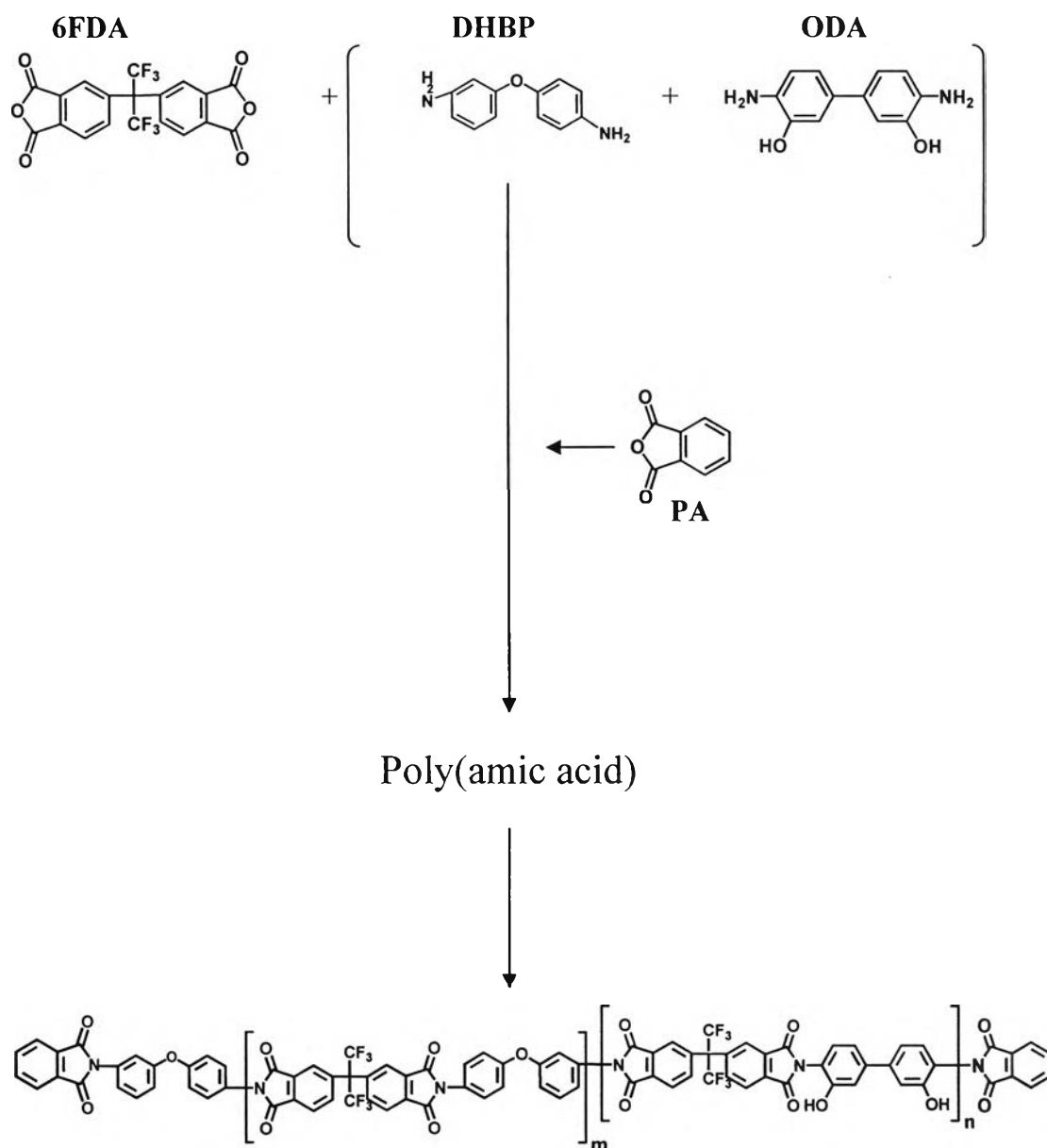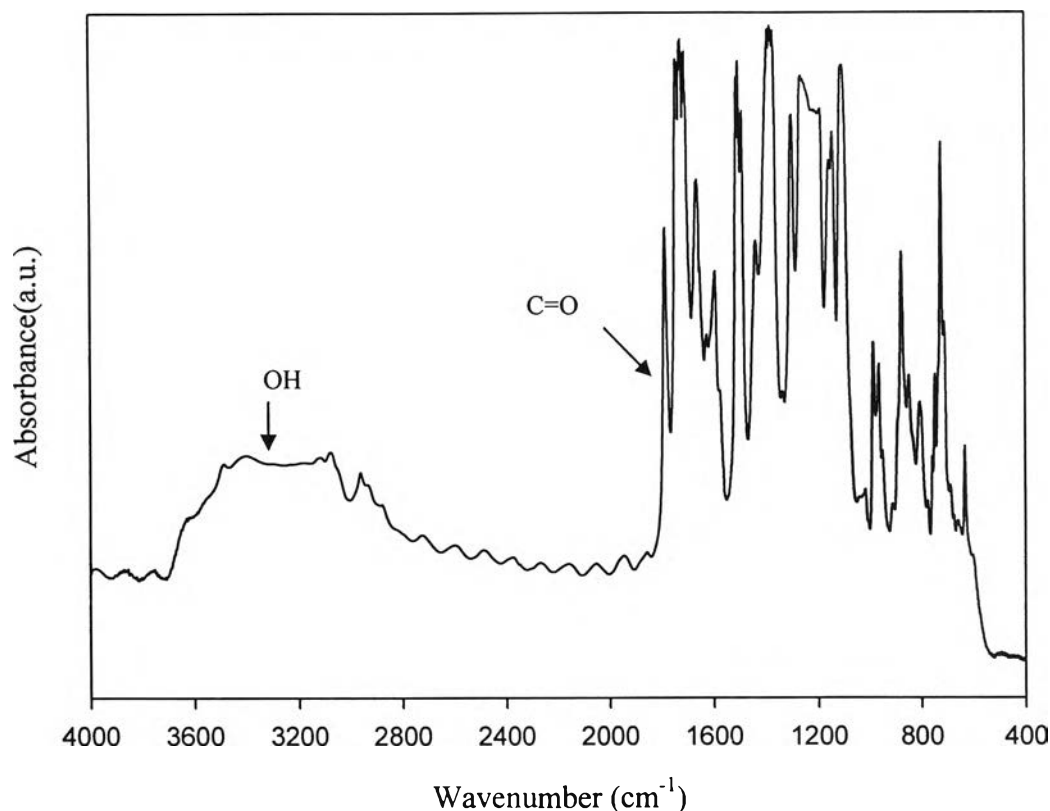
**PA**

Poly(amic acid)

**Figure 5.1** Structure of polyimide.

## 5.1.2 The structure of polyimide

The structures of polyimides were investigated by FT-IR spectra. The solid FT-IR samples of polyimide were prepared via KBr pellet. Figure 5.2 shows a typical FT-IR spectrum of the synthesized polyimide.

**Figure 5.2** FT-IR spectra of hydroxyl polyimide.

From figure 5.2, The characteristic imide groups are observed at 1785 cm$^{-1}$ for C=O asymmetric stretching vibrations, at 1720 cm$^{-1}$ for C=O symmetric stretching vibrations, at 1380 cm$^{-1}$ for C-N stretching vibrations and at 725 cm$^{-1}$ for C=O bending vibrations. The carbonyl group (C=O) in CONH stretching band around 1660 cm$^{-1}$ was not observed in Figure 5.2, which indicates the successful thermal imidization polyimide. The broad absorption around 3400 cm$^{-1}$ is attributed to hydroxyl groups that contained in the main chain by cooperation of the DHBP.

**5.1.3 Preparation of the first layer**

Various amounts of MonoChloroIsobutyl-POSS (POSS-Cl) were directly reacted with reactive hydroxyl groups of polyimide. The concentrations of hydroxyl groups in the polyimide were controlled by adjusting the synthesis ratio of diamine monomers of DHBP that contain two hydroxyl groups and 3,4'-ODA that contain no

hydroxyl groups. The amount of POSS was controlled at constant 10% of the hydroxyl functional groups of polyimide. In other word, the mole ratio of the OH over mole POSS was keep at 1:0.1 and the details of the combination can be seen as below,

**Table 5.2** Content of POSS-Cl in first layer

| Code | mol OH in PI (mol) | mol POSS in PI (mol) | weight POSS in PI (g) |
|------|--------------------|----------------------|-----------------------|
| PI25-L1 | $1.634 \times 10^{-4}$ | $1.634 \times 10^{-5}$ | 0.0153 |
| PI50-L1 | $3.247 \times 10^{-4}$ | $3.247 \times 10^{-5}$ | 0.0304 |
| PI75-L1 | $4.840 \times 10^{-4}$ | $4.840 \times 10^{-5}$ | 0.0453 |
| PI100-L1 | $6.412 \times 10^{-4}$ | $6.412 \times 10^{-5}$ | 0.0600 |
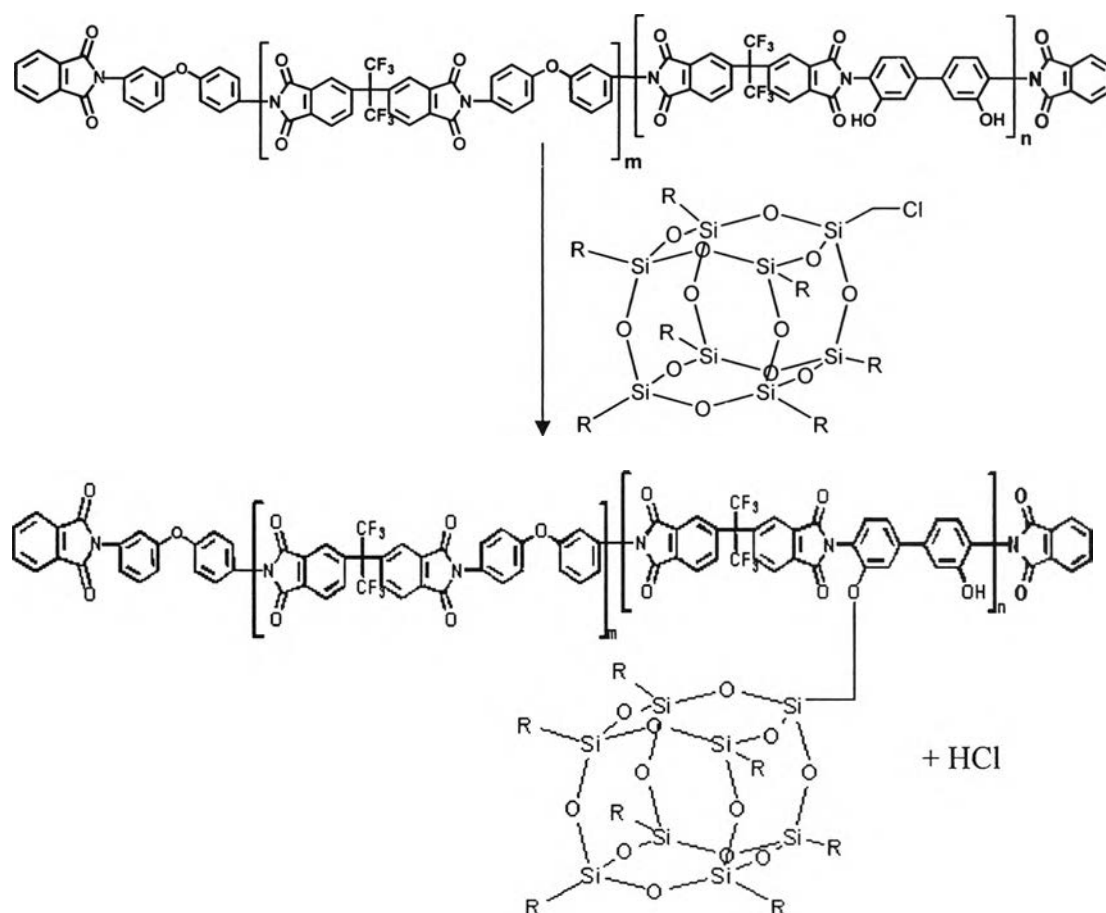


**Figure 5.3** Structure of POSS-polyimide (First layer).

### 5.1.4 The structure of POSS-polyimide (First layer)

The structures of POSS-Polyimide were investigated and confirmed by FT-IR spectra. The solid FT-IR samples of the first layer polyimide were examined via KBr pellet. Figure 5.4 shows a typical FT-IR spectrum of POSS-Cl and Figure 5.5 shows a typical FT-IR spectrum of POSS-Polyimide composite together with synthesized polyimide (before cooperation of POSS) for comparison.
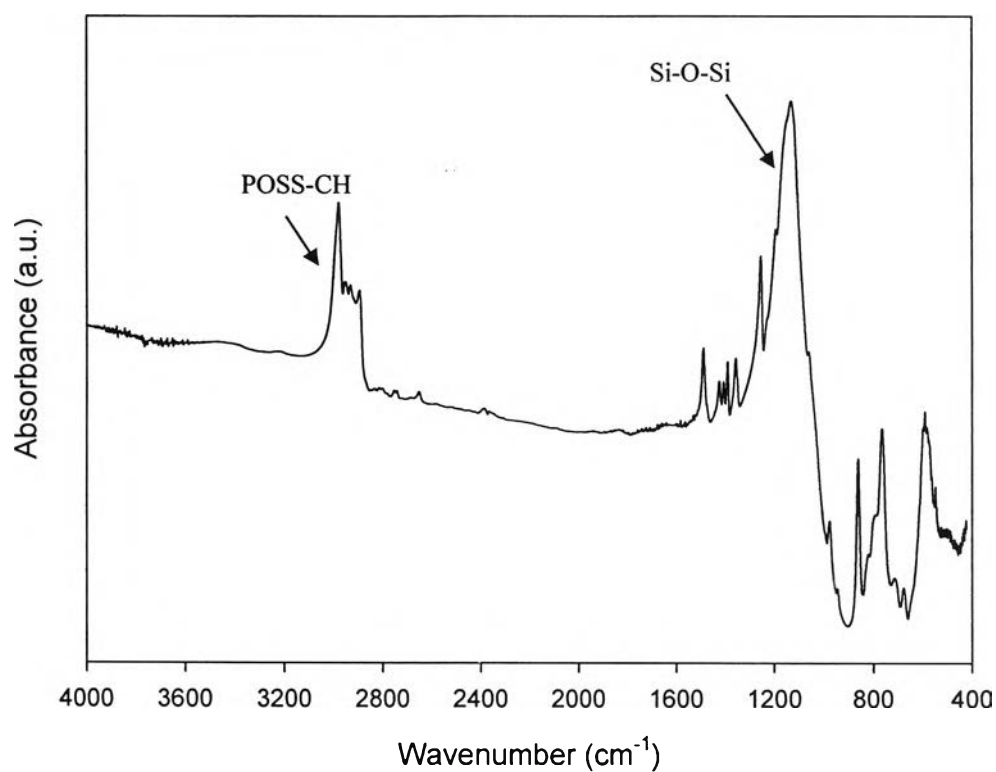


**Figure 5.4** shows a typical FT-IR spectrum of POSS-Cl
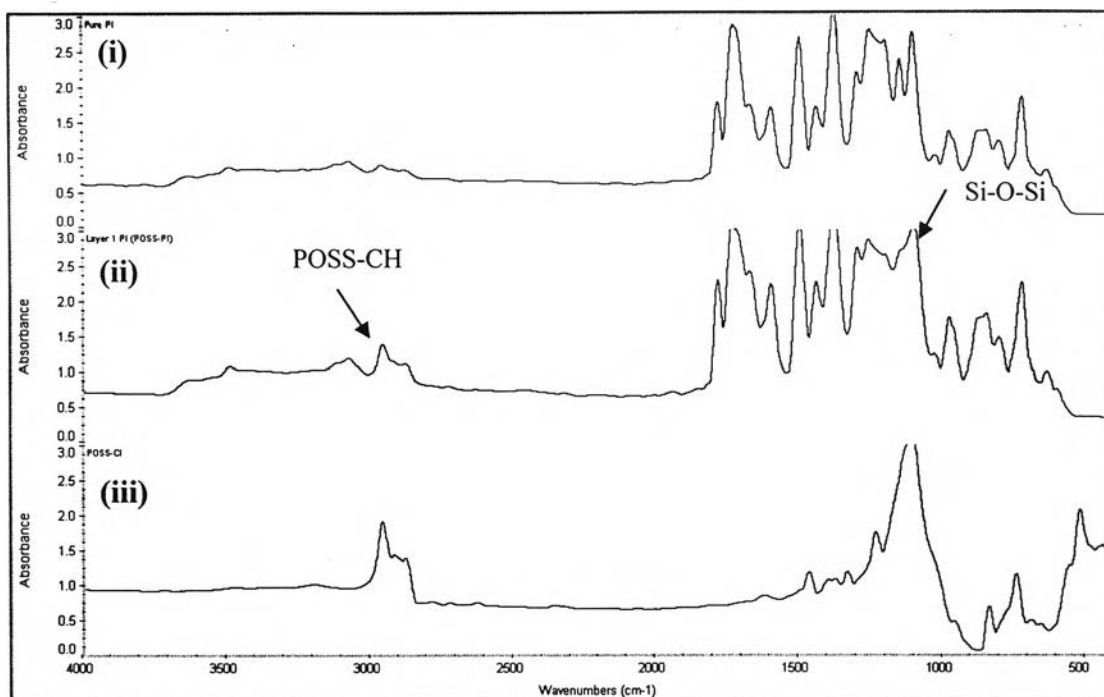
**Figure 5.5** FT-IR spectra of (i) polyimide, (ii) POSS-polyimide (first layer) and (iii) POSS-Cl.

From Figure 5.5, the FT-IR spectra of the first layer and pure polyimide before cooperating POSS were shown. The POSS-Cl will cooperate in to polyimide and the FTIR of the cooperated polyimide shows the peak of the functional groups represent the Si-O-Si asymmetric stretching absorption between 1000 and 1180 cm$^{-1}$ and the aliphatic C-H stretching band between 2800 and 2900 cm$^{-1}$. These characteristic peaks confirm that POSS molecules are incorporated to side chain space of polyimide via the hydroxyl group of DHBP.
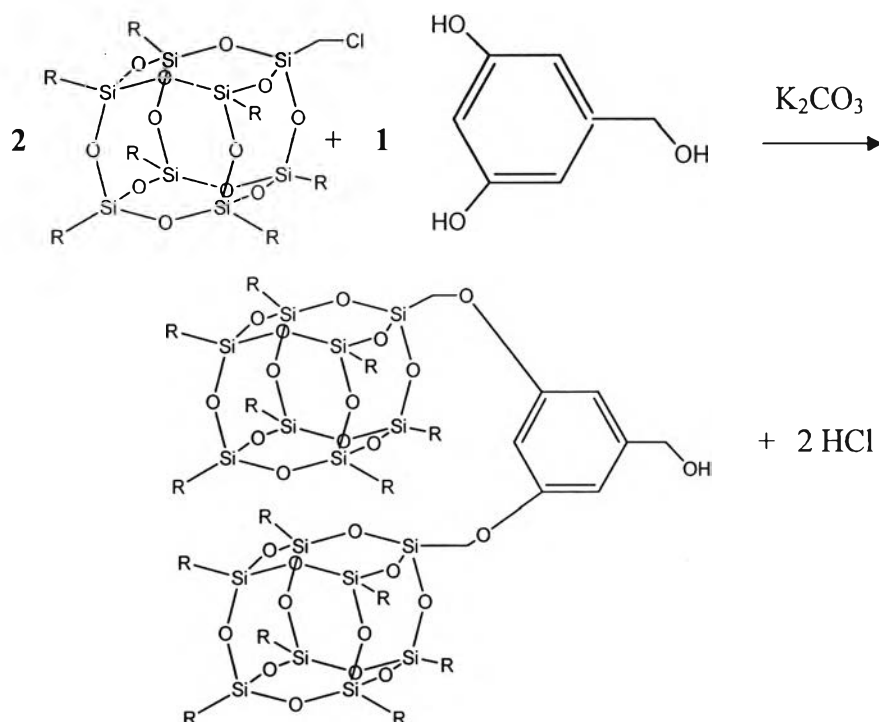
### 5.1.5 Preparation of the second layer

The second layers of hyperbranch polyimide were made from the pure polyimide with the ready made hyperbranch ether. The Br-functional group of the hyperbranch ether will react with the hydroxyl group of polyimide and emit HBr while leaving the oxygen as the ether bond between the ether branch and polyimide.

The ether can be synthesized using the 3,5-Dihydroxybenzyl alcohol (DA) with the POSS-Cl by the molar ratio of 1:2. However the DA has three hydroxyl groups; two groups attached directly to the benzene ring and the last hydroxyl attached with $-CH_2-$ which further directly attached to the benzene ring. The more reactive two hydroxyl groups of DA will react with POSS-Cl and emit two mole HCl. Usually, the dihydroxy that attached to the benzene ring are much more reactive, so the last hydroxyl group that attached to the $-CH_2$-Benzene group were left unreacted. The last hydroxyl group of DA further reacted with $CBr_4$ and $PPh_3$ yield the Br functional group instead of the hydroxyl group of the ether. These Br functional groups will further react with the hydroxyl group of polyimide created the hyperbranch structure and emit HBr as results. In other word, one hydroxyl of the polyimide will be attached to the ether bond linked the benzene ring with the main chain and that benzene ring linked to the ether and two POSS molecules.

The amount of the branch and the hydroxyl group on polyimide was kept constant. The detail of the compositions of POSS and the second layer made can be summarized in the following table.

**Table 5.3** Content of POSS-Cl in second layer

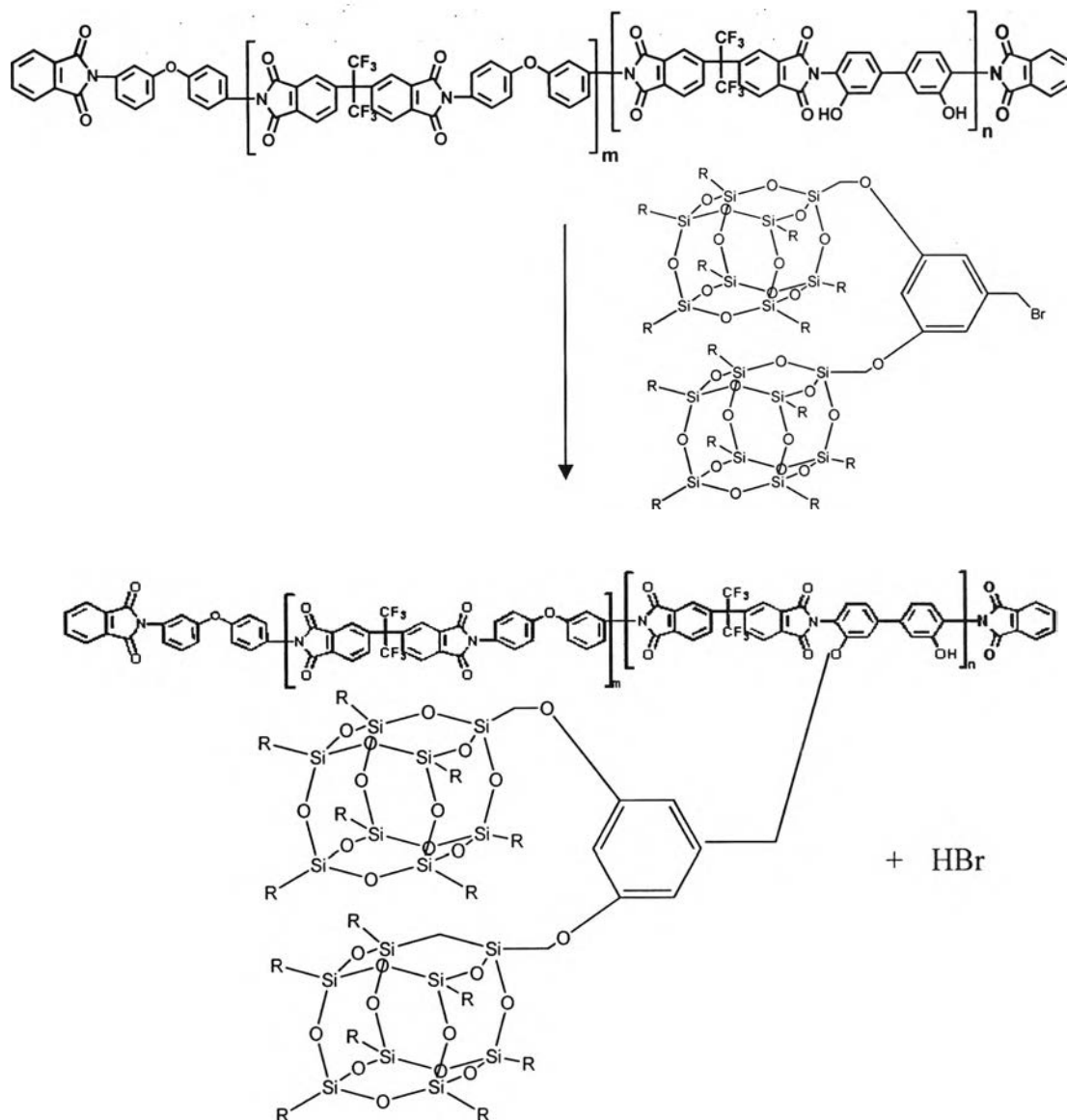| Code | mol OH in PI (mol) | mol Br in PI (mol) | mole POSS in PI (mol) |
|------|------|------|------|
| PI25-L2 | $1.634 \times 10^{-4}$ | $4.086 \times 10^{-6}$ | $8.172 \times 10^{-6}$ |
| PI50-L2 | $3.247 \times 10^{-4}$ | $8.121 \times 10^{-6}$ | $1.624 \times 10^{-5}$ |
| PI75-L2 | $4.840 \times 10^{-4}$ | $1.211 \times 10^{-5}$ | $2.421 \times 10^{-5}$ |
| PI100-L2 | $6.412 \times 10^{-4}$ | $1.604 \times 10^{-5}$ | $3.208 \times 10^{-5}$ |

**Figure 5.6** Structure of dendritic benzyl alcohols, [G-1] OH (Second layer)
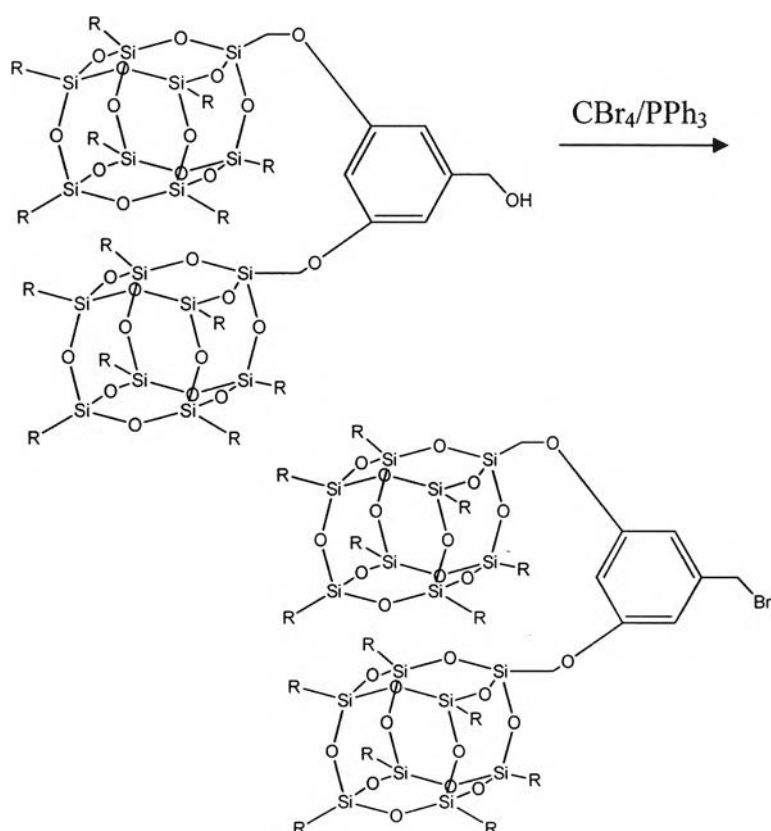


**Figure 5.7** Structure of dendritic benzyl, [G-1] Br (Second layer)

**Figure 5.8** Structure of hyperbranch polyether on polyimide (Second layer)

### 5.1.6 Preparation of the third layer

In stead of reaction of the ether branch in the second layer with the polyimide main chain, the Br second layer branch will react with the DA again. By the same chemical method explained in the above subjected, the third layer branch ether can be made. Four POSS molecules were attached to the two layer of DA and the last hydroxyl group of DA will be further reacted with $CBr_4$ and $PPh_3$ and changed in to Br. The Br ether branches obtained were finally attached to the hydroxyl at the polyimide main chained. In other word, the four POSS-Cl molecules will be attached

with ether and benzene ring which still be attached to the ether and other benzene ring before attached the ether linkage to the main chain polyimide.

The amount of the branch and the hydroxyl group on polyimide was kept constant. The detail of the compositions of POSS and the third layer made can be summarized in the following table.

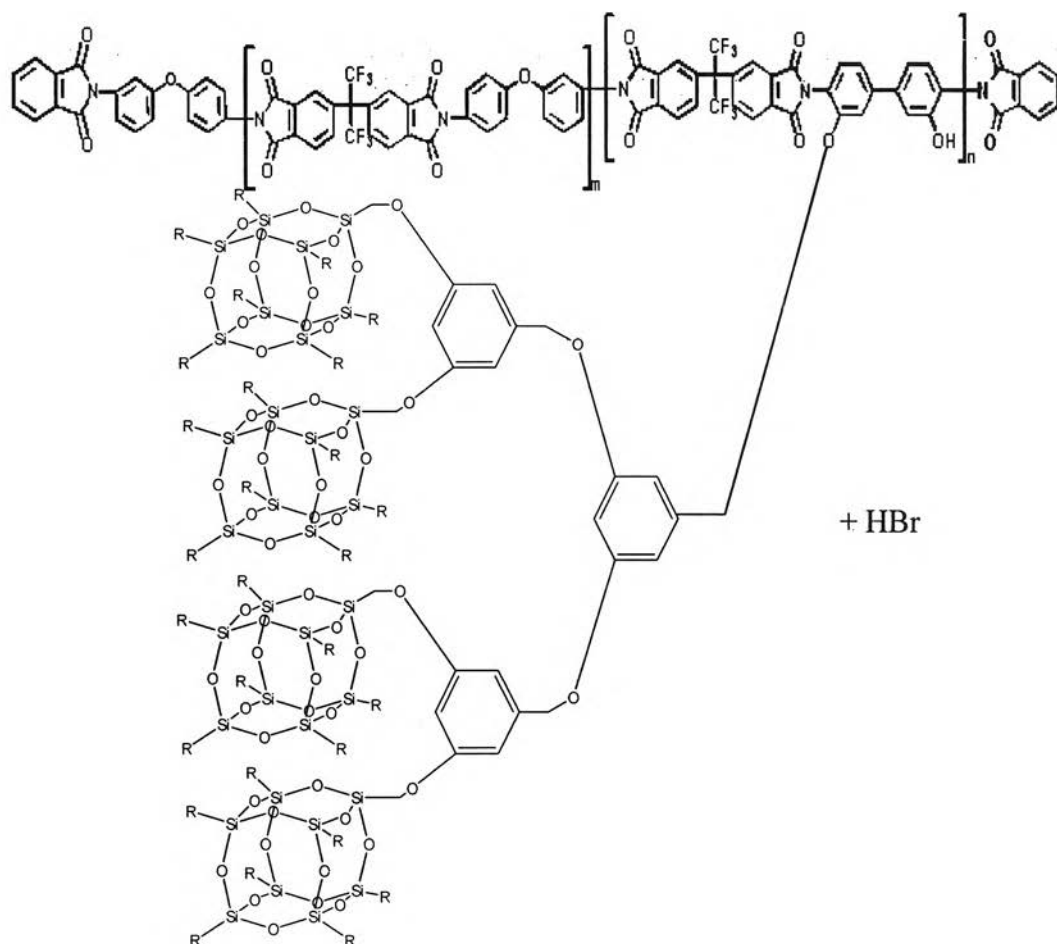**Table 5.4** Content of POSS-Cl in the third layer

| Code | mol OH in PI (mol) | mol Br in PI (mol) | mole POSS in PI (mol) |
|------|--------------------|--------------------|-----------------------|
| PI25-L3 | $1.634 \times 10^{-4}$ | $1.023 \times 10^{-6}$ | $4.094 \times 10^{-6}$ |
| PI50-L3 | $3.247 \times 10^{-4}$ | $2.028 \times 10^{-6}$ | $8.113 \times 10^{-6}$ |
| PI75-L3 | $4.840 \times 10^{-4}$ | $3.026 \times 10^{-6}$ | $1.211 \times 10^{-5}$ |
| PI100-L3 | $6.412 \times 10^{-4}$ | $4.006 \times 10^{-6}$ | $1.602 \times 10^{-5}$ |
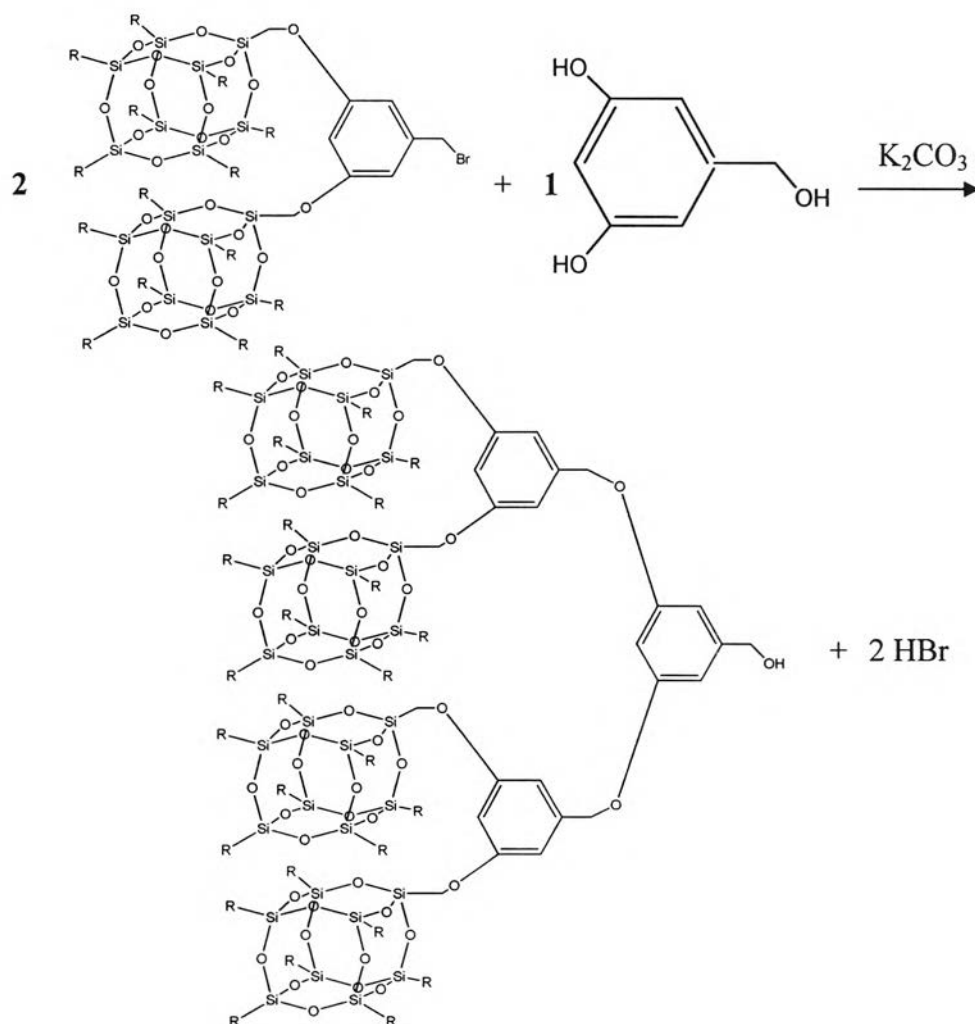


**Figure 5.9** Structure of dendritic benzyl alcohols,[G-2]OH (Third layer)
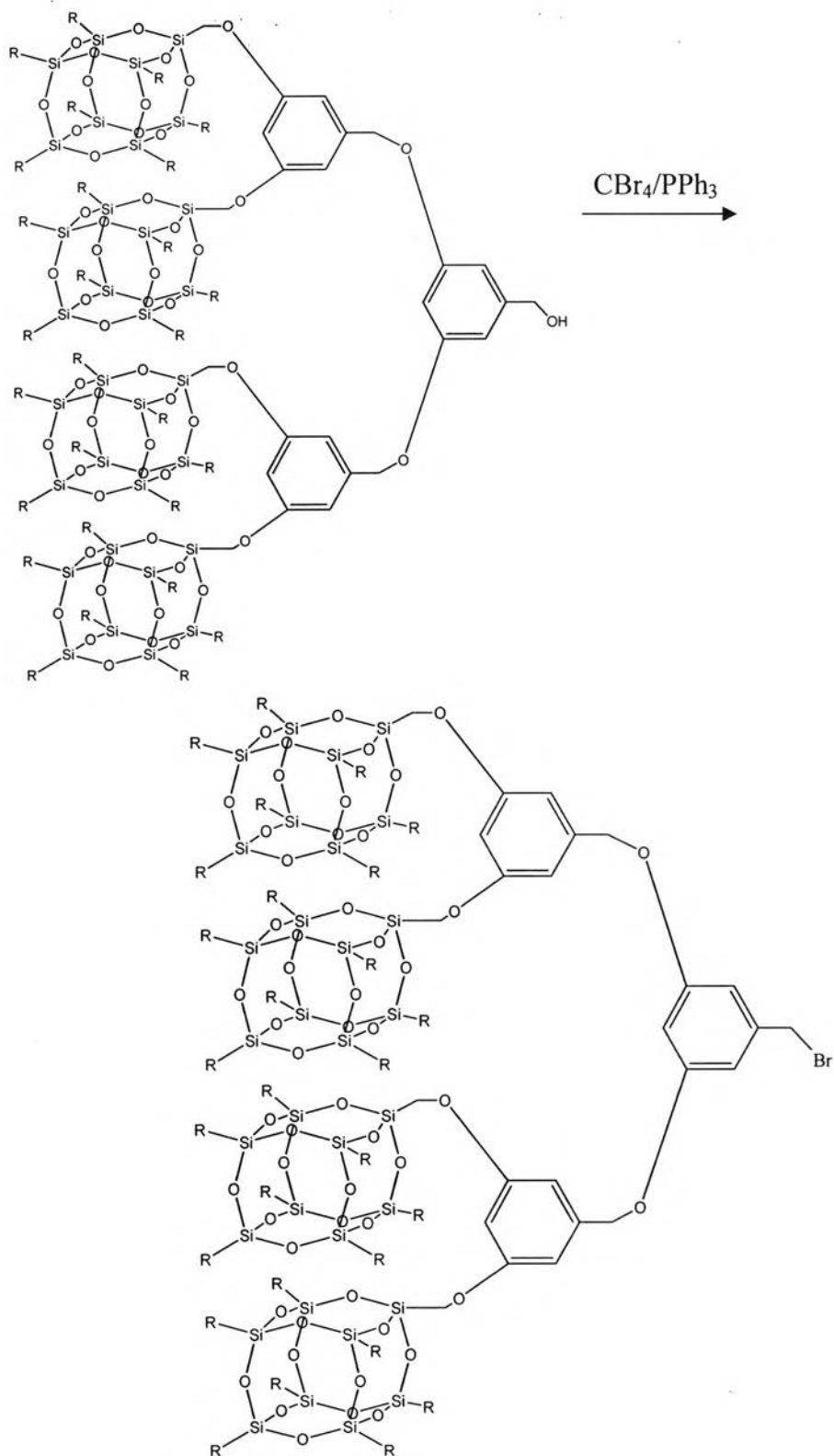
**Figure 5.10** Structure of dendritic benzyl,[G-2]Br (Third layer)

**Figure 5.11** Structure of hyperbranch polyether on polyimide (Third layer)

### 5.1.7 The structure of hyperbranch polyether on polyimide

The structures of hyperbranch polyether on polyimide were investigated and confirmed by FT-IR spectra. The solid FT-IR samples of the second and third layers polyimide were examined via KBr pellet. Figure 5.12 shows a typical FT-IR spectrum of hyperbranch polyether on polyimide together with synthesized polyimide (before cooperation of hyperbranch polyether) for comparison.
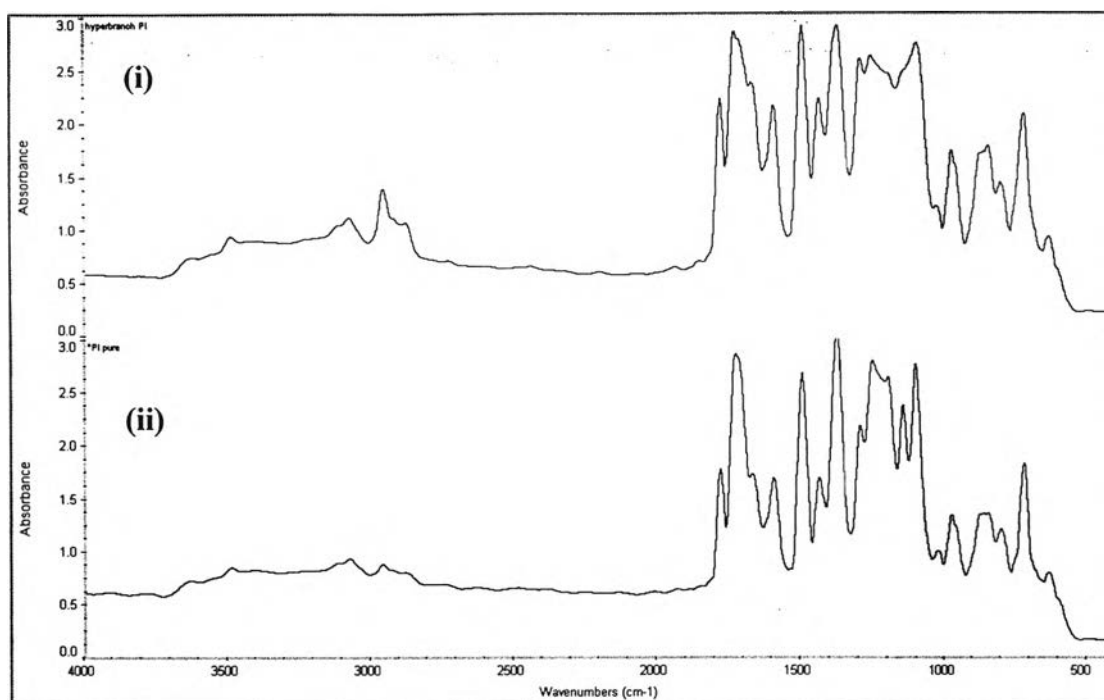
**Figure 5.12** shows a typical FT-IR spectrum of hyperbranch polyimide of (i) hyperbranch polyimide, (ii) polyimide

From Figure 5.12 represented the FT-IR spectra of hyperbranch polyimide and pure polyimide before cooperating hyperbranch were shown. The FT-IR of the hyperbranch polyimide show the peak of the ether groups represent the asymmetrical C-O-C stretching at 1275-1200 cm$^{-1}$ and symmetrical stretching near 1075-1020 cm$^{-1}$. These characteristic peaks confirm that hyperbranch molecules are incorporated to side chain space of polyimide via the hydroxyl group of DHBP.

## 5.2 Thermal properties

### 5.2.1 Influence of various layer of polyimide on thermal properties

The thermal properties of the films were investigated by TGA under oxygen and nitrogen atmosphere. The thermal stabilities of synthesized hyperbranch POSS-PI were reduced because of the addition of aliphatic linkage on the side chain and the ether linkage that combined in hyperbranch ether. General, degradation temperatures (Td) of POSS-polyimide nanocomposites are lower than that of pure polyimide,

because of the degradation of POSS molecules that contain some benzene ring (at ~ 400 °C). Moreover, the aliphatic linkages (Ph-CH$_2$-O-Ph) in hyperbranch polyether have low degradation temperatures (Td) about 250 °C. The ether in hyperbranch will degrade at higher temperature than the aliphatic linkages because no early loss weight from the first layer which also contain some ether but no aliphatic linkages degrade at higher temperature than the second and third layer that contain aliphatic linkages.
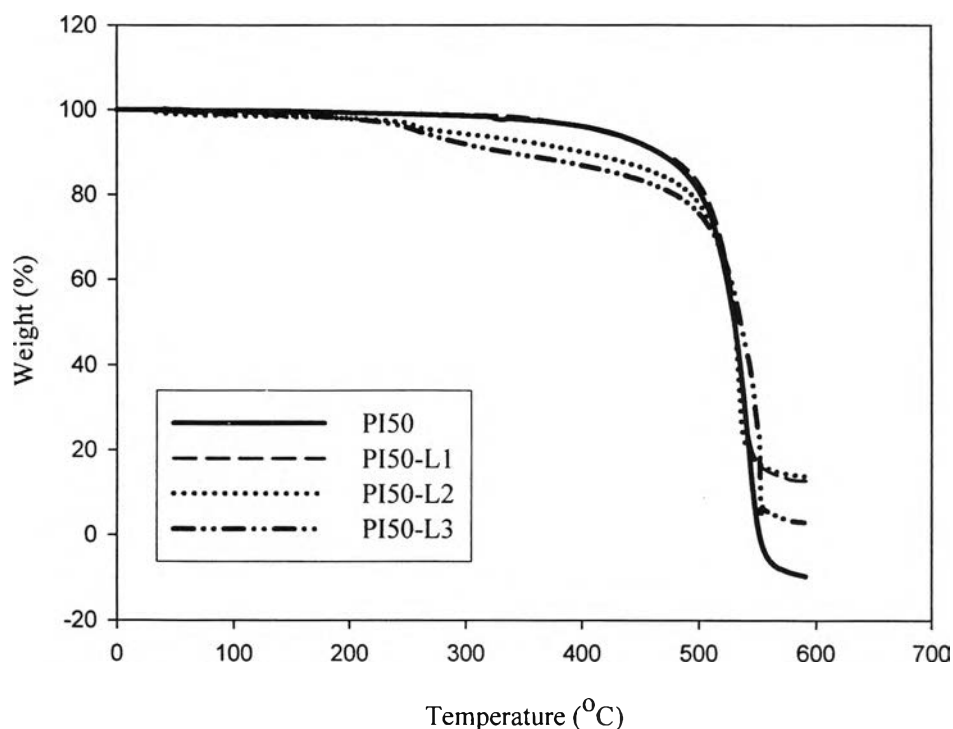


**Figure 5.13** TGA curve of pure polyimide, layer1, layer2 and layer3 in O$_2$

For example, in the case of PI50, we can see the degradations of layer2 and layer3 occurred in two stages. The first stage is the aliphatic linkages degradation that appeared about 250 °C and the second stage appeared above 500 °C because of the degradation of the imide backbone. The first layer (POSS-PI) has slightly lower degradation characteristic than the pure PI due to the ether linkage in POSS branch structures. So, these data indicate that the heat resistance of polyimide in the order of pure PI 〉 layer1 〉 layer2 〉 layer3 respectively.
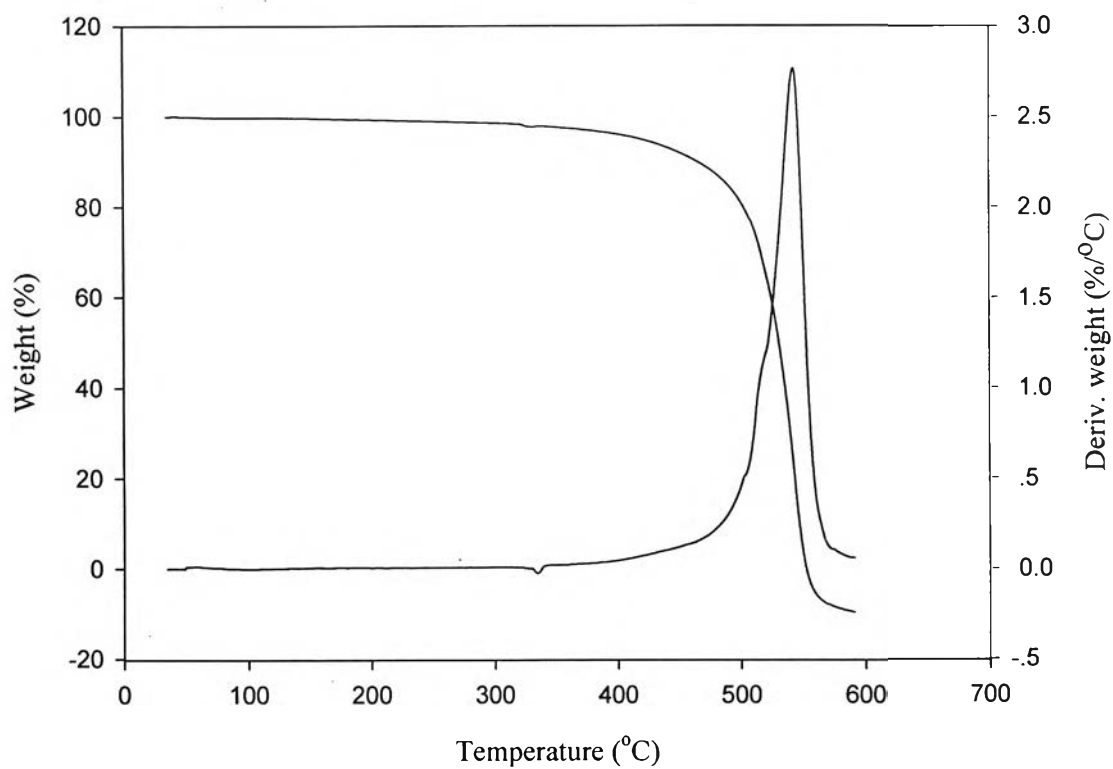
**Figure 5.14** TGA curves of pure polyimide in $O_2$

From figure 5.14, we can see the decomposition temperature of pure polyimide appeared above 500°C that imply the good thermal stability of polyimide.
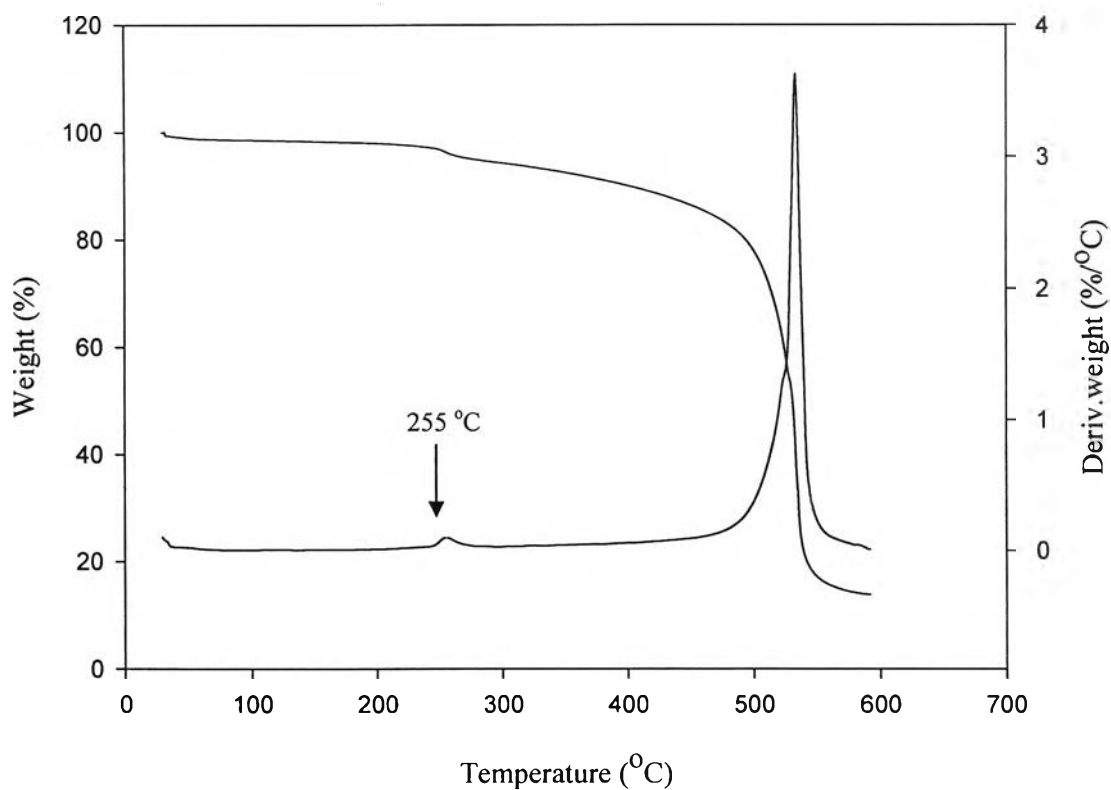
**Figure 5.15** TGA curve of hyperbranch polyimide in $O_2$

The differences in Figure 5.14 and Figure 5.15 are the transition at 255°C.

Figure 5.15 shows the early stage degradation at 255 °C due to the aliphatic linkages

degradation in hyperbranch polyimide. The final stage degradation shows the

transition above 500 °C because of the degradation of imide backbone as same as the

polyimide in Figure 5.14.

**Table 5.5** Summary of the degradation temperature of various layers

| Code | Td5% (°C) in $O_2$* | Td 10% (°C) in $O_2$* |
|---|---|---|
| PI50-L0 | 419 | 465 |
| PI50-L1 | 414 | 466 |
| PI50-L2 | 259 | 335 |
| PI50-L3 | 232 | 286 |
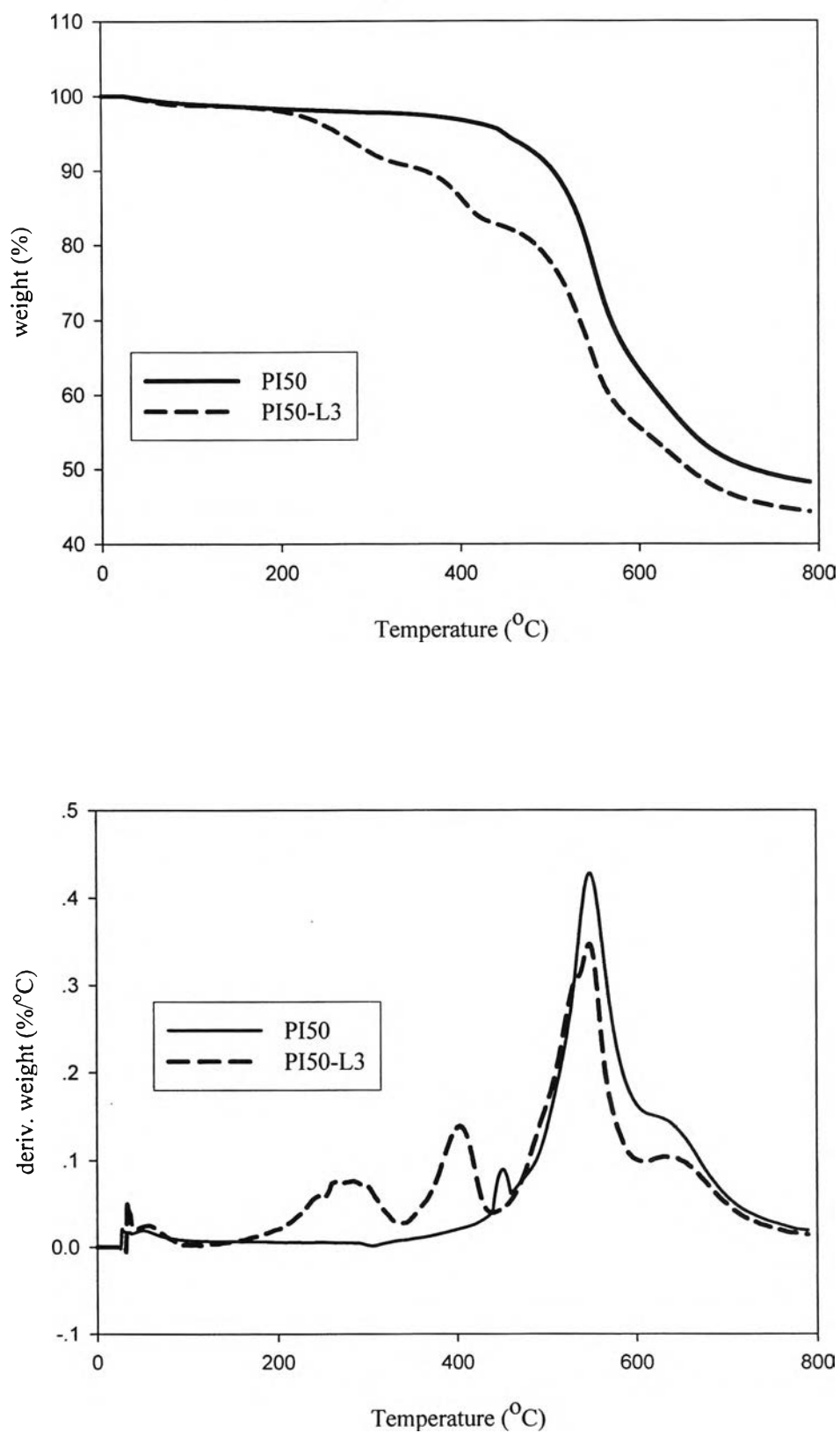
**Figure 5.16** TGA curve of pure polyimide and layer 3 in $N_2$

From the TGA thermograms, it was seen that PI50 exhibited a degradation temperature (5% weight loss) at 449°C and degradation temperature (10 % weight loss) was about 504°C and PI50-L3 shown the values of 265°C and 359°C respectively. Char yield of the PI50 reported at 800°C was 48.29% by weight and the PI50-L3 reported at 800°C was approximately 44.36% by weight. This can be explained that the aliphatic ether linkage in hyperbranch component in PI50-L3 was burn about 250°C due to the stronger of ether bond was lower imide bond. Addition, the hyperbranch have POSS molecules that is included isobutyl and benzene ring which can further degradation.

**Table 5.6** Thermal properties of the polyimide films

| Code | Thermal properties | | |
|---|---|---|---|
| | T 5% (°C)[a] | T 10% (°C)[b] | Char yield (%)[c] |
| PI50 | 449 | 504 | 48.29 |
| PI50-L3 | 265 | 359 | 44.36 |

[a] The temperature where 5% weight loss occurred.

[b] The temperature where 10% weight loss occurred.

[c] Weight of residue polyimide at 800°C.

## 5.3 Mechanical properties

### 5.3.1 Influence of various layers on Dynamic mechanical properties

The dynamic mechanical properties of various layers hyperbranch polyimide in were investigated by DMA. The rectangular specimens under tension mode were applied for DMA. The temperature range was between 50 to 450°C under nitrogen atmosphere. The tension mode of DMA can be measured at various frequencies, but the obtained at frequency 1 Hz was selected to represent the mechanical properties. The dynamic mechanical properties of the polyimide films were performed as a function of temperature. Figure 5.17, Figure 5.18 and Figure 5.19 represent the loss modulus, the storage modulus and tan δ of the polyimide films respectively.
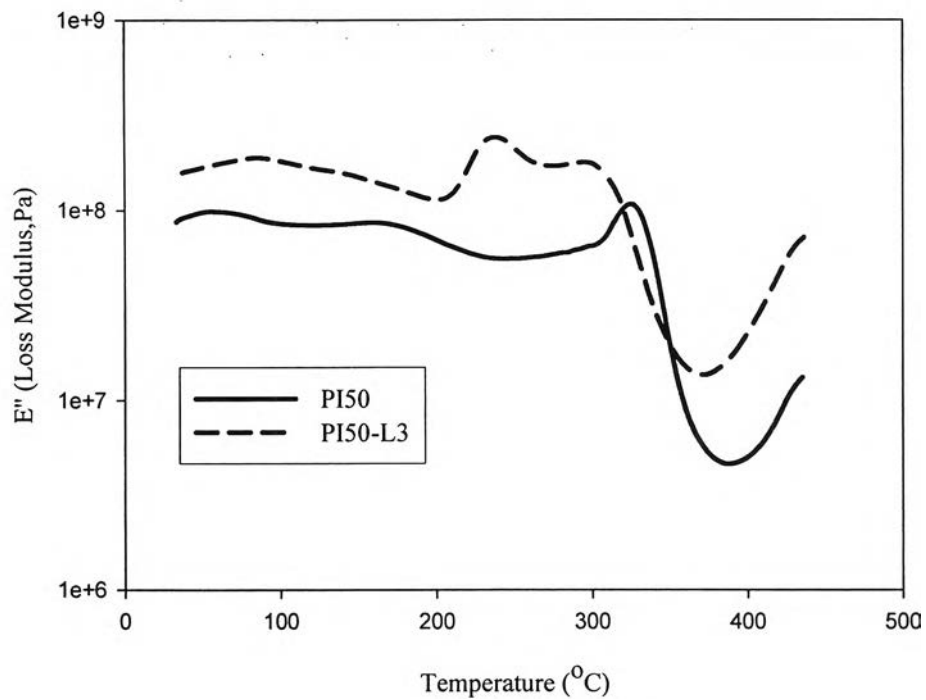
**Figure 5.17** DMA curves (loss modulus (E'') and temperature) for PI50 and PI50-L3
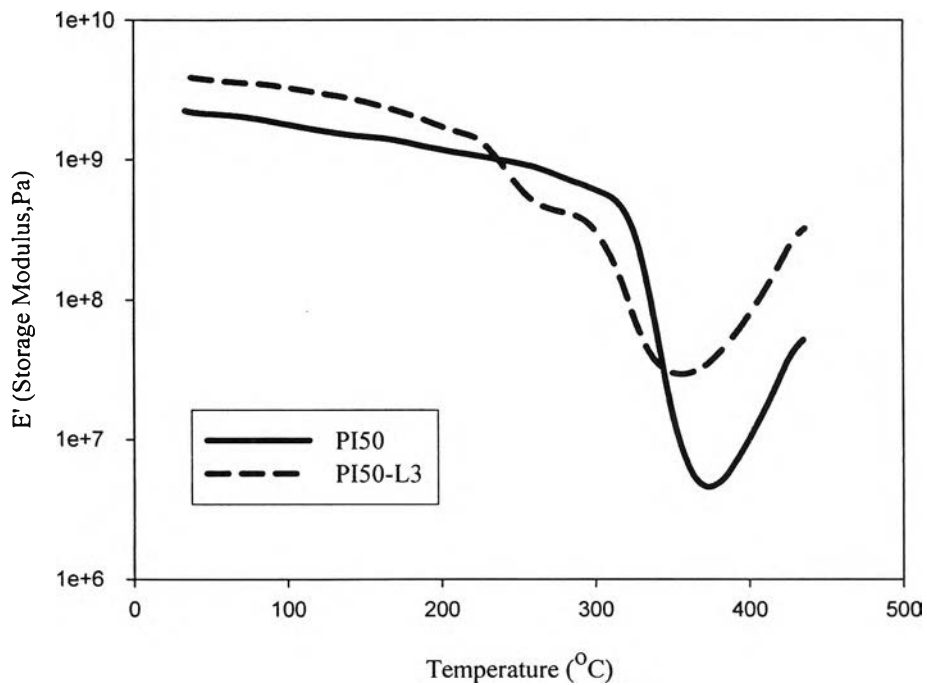


**Figure 5.18** DMA curves (storage modulus (E') and temperature) for PI50 and PI50-L3
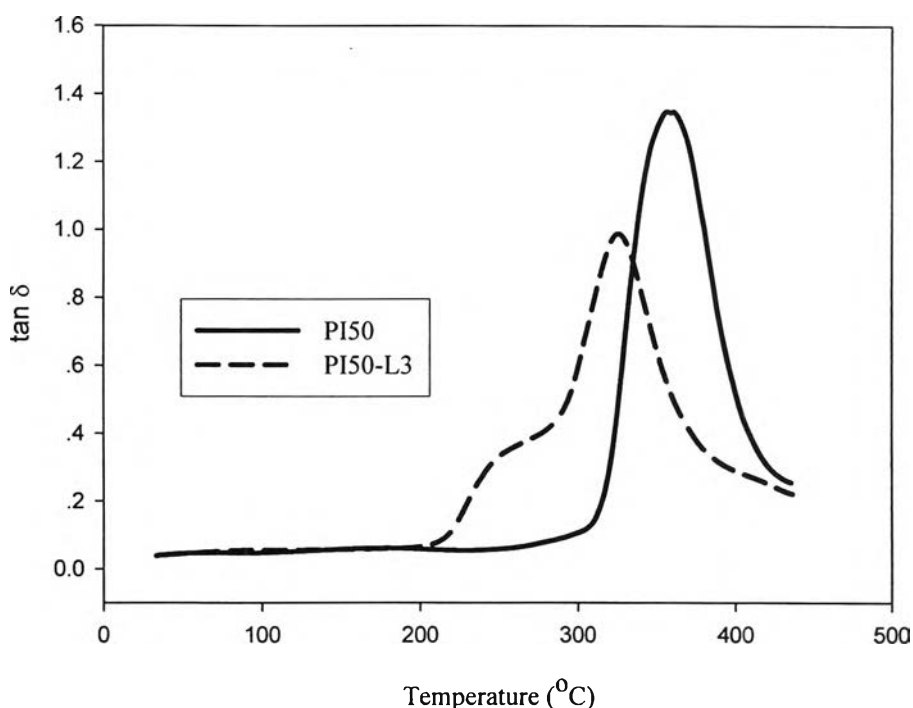
**Figure 5.19** DMA curves (tanδ and temperature) for PI50 and PI50-L3

It could be observed that the storage modulus and loss modulus of the PI50-L3 were lower with PI50 in the temperature range of 200-450 °C.The large decrease in the storage modulus at temperature above 330°C indicated the beginning of the decrease strength. In the PI50-L3 exhibited higher the storage modulus and loss modulus than the PI50. The PI50-L3 has two relaxation due to ether groups in structure.

From tan δ curves, the glass transition temperature of PI50 and PI50-L3 displayed 356.59°C and 324.64°C respectively. The lower glass transition temperature was due to hyperbranch structure which has presence of POSS organic and ether within the polyimide network and thus increases the free volume of the polyimide matrix. The reduction in Tg imply the easier mobility of the main chains that has the ether attached than the pure PI. Even increase the layer to the third layer, the Tg of the second layer is comparable to the Tg of the third layer. The comparable Tg imply the same mobility of the main chains regardless of the ether layer.

### 5.3.2 Influence of various layers on tensile mechanical properties

The tensile mechanical properties were measured by tensile testing machine at room temperature and each sample of polyimide films. Figure 5.20 and Figure 5.21 show the tensile stress and tensile strain of PI50 and PI50-L3 respectively.
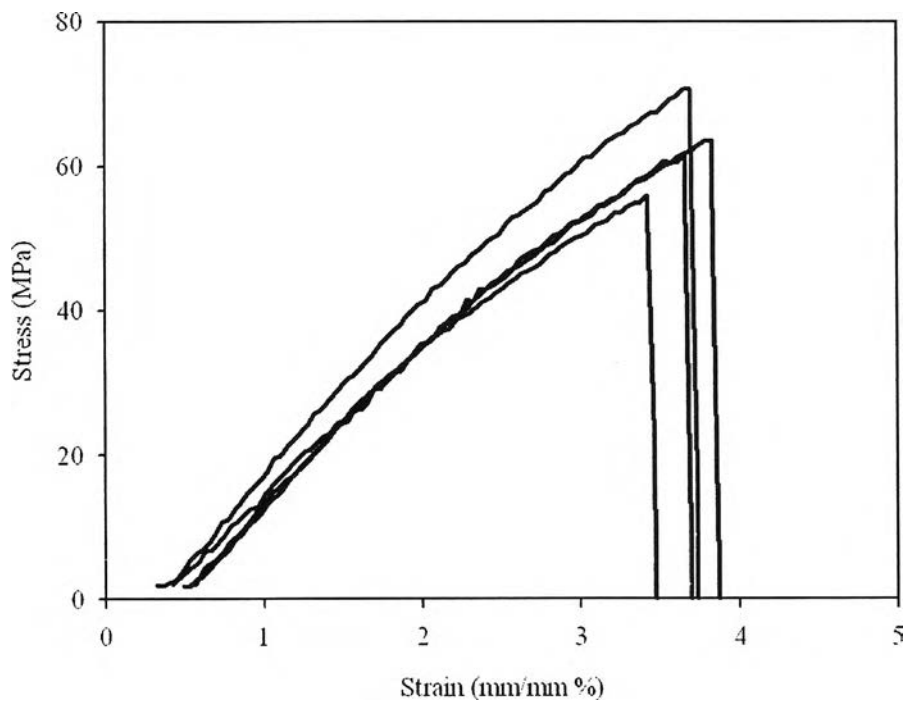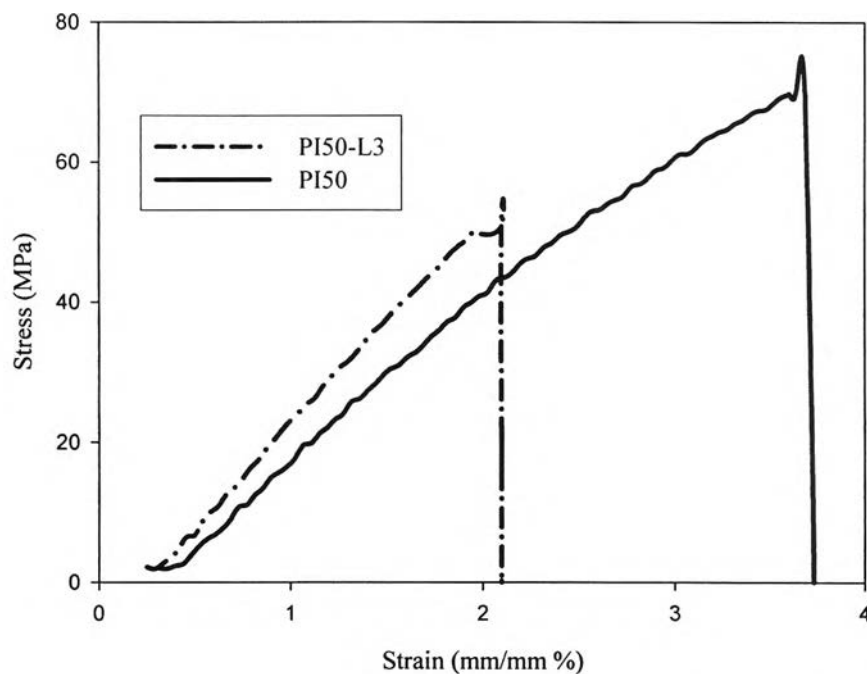


**Figure 5.20** Tensile strength of PI50
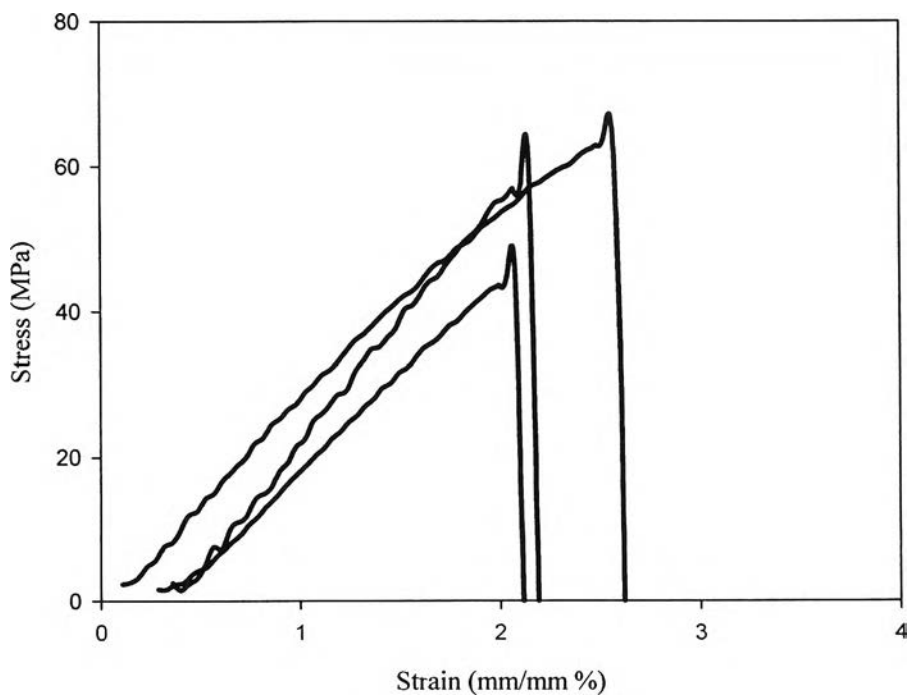


**Figure 5.21** Tensile strength of PI50-L3

**Figure 5.22** Comparison of Tensile strength of PI50 and PI50-L3

**Table 5.7** Tensile properties of PI50 and PI50-L3

| Code | Tensile properties | | |
|---|---|---|---|
| | Tensile stress at Break (Standard) (MPa) | Modulus (E-modulus) (MPa) | Toughness[a] (MPa) |
| PI50 | 65.2 | 2,357 | 133.7 |
| PI50-L3 | 51.9 | 2,730 | 47.93 |

[a] Calculated by the area under stress-strain curve.

The results of tensile stress tests of the PI50 and the PI50-L3 are shown in Figure 5.22 and Table 5.7. By comparing with PI50 and PI50-L3, the PI50 exhibited the higher tensile strength than PI50-L3. This can also be explained due to hyperbranch structure and POSS matrix created porous silsesquioxane nanocores, led to the reduction increase free volume and loosing polyimide conformation.

Additionally, the PI50-L3 exhibited the lower elongation at break, the lower toughness and the higher modulus than the PI50.

## 5.4 Dielectric properties

The dielectric properties of various layers polyimide were investigated by LCR meter. All samples were treat in vacuum oven in 100 °C before measured because dielectric constant depend moisture of samples. Table 5.8 and Figure 5.23 show the dielectric constants of the polyimide films calculated by the following equation:

$$k = \frac{Ct}{\varepsilon_0 A}$$

where C is the measured capacitance, t is the thickness of the sample, A is the area of the film and $\varepsilon_0$ is the permittivity of the free space ($8.854 \times 10^{-12}$ MKS unit).

**Table 5.8** Dielectric constant of polyimide films

| Code | Dielectric constant at 1 MHz | | | |
|---|---|---|---|---|
| | L0 | L1 | L2 | L3 |
| PI25 | 3.17 | 3.13 | 3.08 | 2.81 |
| PI50 | 3.22 | 3.09 | 2.88 | 2.54 |
| PI75 | 3.40 | 3.17 | 3.04 | 2.73 |
| PI100 | 3.55 | 3.16 | 2.99 | 2.63 |
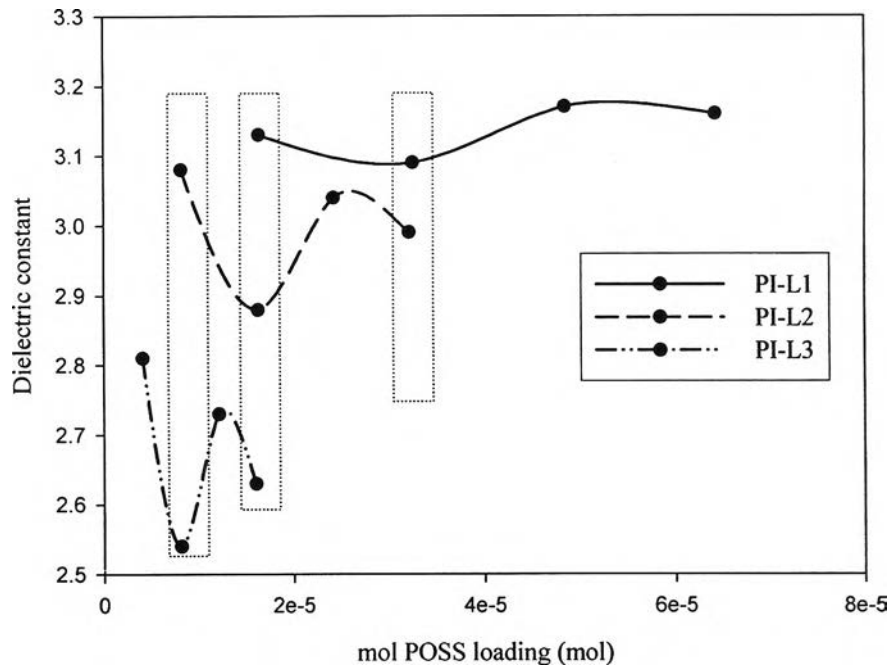
**Figure 5.23** shows content of mol POSS loading and dielectric constant

Figure 5.23 shows the dielectric properties against the amount of POSS in the samples. Actually the ratio of the occupied hydroxyl group of polyimide to the available hydroxyl in the molecules was kept constant. Moreover the amount of POSS in the first layer is twice of the second layer and the amount of POSS in the third layers is half of the second layer. In other word, the amount of POSS in the samples were reduces half in each layer. Fortunately, if we measured the net incorporate POSS in the samples, the variation of the dielectric constant of the same amount of POSS in the molecules can be compared as follows; the four points in each layer show the percent of the hydroxyl in the main chain from 100, 75, 50 and 25 from right to left respectively. Because the ratios of the hydroxyl occupied against the total hydroxyl in the main chain are kept constants, the highest concentration of POSS in the samples is reduced from PI100, PI75, PI50 and PI25 respectively. The same tendency of increasing the POSS and reducing the dielectric constant can be applied in all layers. (L0, L1, L2, and L3) In other word, the more is the incorporated POSS, the less is the dielectric constant regardless of the amount of layer applied. The reduction in the dielectric constant by POSS results from the low dielectric constant of POSS

molecules (k=2.1) and the higher free volume by the incorporation of POSS in the main chain PI.

If the same amount of POSS in different layer was compared. The third layer has the lowest dielectric constant, the second layer dielectric constant is higher than the third layer but still lower than the first layer and the first layer has the highest dielectric constant. In other word, the more is the layer, the less is the dielectric constant. Because the same amount of POSS applied, so the different should come from the difference in the branches. These various layers will create more free volumes to the samples and the more the free volumes, the less the dielectric constant.

From table 5.8 and figure 5.23, the important conclusion can be drawn. If the same amount of the total hydroxyl were compared (i.e. PI100), the effects of reduction in dielectric constant rely on the layer more than the concentration of the POSS. If the right points in each layer in Figure 5.23 were compared (PI100), the PI100-L1 has the concentration of POSS in the samples twice of the concentration of the POSS in the PI100-L2 and PI100-L1 has the concentration of POSS in the samples four times the concentration of the POSS in the PI100-L3. However, the less POSS should results in higher dielectric constant, but from our experimental data, the dielectric constant of the PI100-L3 is lower than the PI100-L2 and the dielectric constant of the PI100-L2 is lower than the PI100-L1. In other words, the higher is the branch; the lower is the dielectric constant, even the four times reduction of POSS in the samples. More over, this situation is still true regardless of the amount of total hydroxyl in the molecules. (i.e. PI25, PI50, PI75)

The mechanism in reduction of the dielectric constant can be proved by the densities. From the table 5.9, the density of the lower dielectric constant sample in this research is lower. The first assumption comes from the POSS characteristics. The higher POSS molecule will insert the free volumes in the samples and the dielectric and the density were also dropped. The second assumption comes from the branch characteristics. The higher branches will create even more free volume in the samples and the dielectric and the density were also dropped. This mechanism can be applied to this entire thesis and proven to be true by our data.

Table 5.9 Density of polyimide films

| Code | Density of various polyimide films | | | |
|---|---|---|---|---|
| | L0 | L1 | L2 | L3 |
| PI25 | 1.44 | 1.37 | 1.28 | 1.26 |
| PI50 | 1.43 | 1.32 | 1.25 | 1.19 |
| PI75 | 1.43 | 1.34 | 1.27 | 1.23 |
| PI100 | 1.42 | 1.34 | 1.23 | 1.20 |

## 5.5 Solubility

In general, the most important properties of hyperbranched polymers over their linear analogs are the higher solubility, low solution viscosity and higher surface reactivity. These improved properties are mainly due to branched and denser molecular structure with large number of surface groups.

Table 5.10 Solubility of pure polyimide and various layers of polyimide

| Solvent | PI-L0 | PI-L1 | PI-L2 | PI-L3 |
|---|---|---|---|---|
| NMP | oo | oo | oo | oo |
| DMAc | oo | oo | oo | oo |
| m-cresol | o | o | oo | oo |
| CHCl₃ | oo | oo | oo | oo |
| THF | oo | oo | oo | oo |
| Acetone | oo | oo | oo* | oo* |
| Toluene | x | x | o | o |
| methanol | x | x | x | x |
| water | x | x | x | x |

oo = soluble, o = partially soluble, x = insoluble

oo* = rapidly soluble within 30 minutes.

From table 5.10, the solubility of polyimide and various layers of polyimide are concluded. The hyperbranch polyimides have better solubility than the pure

polyimide due to the branched structure. This situation is pronounced in the Toluene, Acetone and m-cresol. The branch polyimide will dissolve easily compare to the first layer and the pure polyimide. The polar aprotic solvents of NMP, DMAc and normal solvent of THF, Chloroform can dissolve the polymer regardless of the degree of branching and the small molecule solvent of water and methanol cannot dissolve the polymer regardless of the degree of branching.