# Organic-Inorganic Hybrids of Polyimide and In-situ Formed Inorganics

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**Abstract:** A number of organic-inorganic hybrids were prepared from polyimide (PI) and polydimethylsiloxane (PDMS). PI was made from poly(amide acid) (PAA) of 3, 3′, 4, 4′-biphenyltetracarboxylic dianhydride (BPDA) and p-phenylenediamine (PDA). PDMS was prepared from diethoxydimethylsilane (DEDMS) through in-situ sol-gel process. The chemical structures of the hybrids were characterized by infra-red spectrophotometer. Scanning electron microscope was used to confirm the particle size of inorganics in the hybrids. Differential scanning calorimetry, thermogravimetric analysis, viscoelastometer and stress-strain tests were used to measure the performance of the PI-PDMS hybrid films. The PI-PDMS hybrids containing 3% PDMS provided higher thermal and mechanical properties than the pristine PI. PI-silica-PDMS hybrids were prepared then with different ratio of silica and PDMS through the in-situ sol-gel process. PI-silica-PDMS hybrids remarkably increased the thermal and mechanical properties of the PI.
**Keywords:** Polyimide, Hybrid, In-situ polymerization, Sol-gel process.

## 1. INTRODUCTION

Aromatic polyimides (PI) exhibit outstanding thermomechanical and dielectrical properties, and now are extensively used in various sectors like microelectronics, aviation industry, aerospace investigation, polymeric separation membrane etc. Research interests in PI have increased in response to the increase of high technology applications. Polymer-inorganic hybrids have been extensively studied to enhance various properties. As inorganics, clay and silica are most often used. It was found that the dispersing of nanolayered clay, in the form of intercalation or exfoliation, into various PI matrices increase the thermal stability, gas barrier property, flame resistance and corrosion protection but decrease the elongation and toughness [1]. PI-silica hybrid is another approach to promote properties of PI. PI and silica from tetraethoxysilane (TEOS) by sol-gel process provide hybrids which have pronounced mechanical and thermal properties, but the hybrid become brittle [2].

It is expected that the introduction of polydimethylsiloxane (PDMS) into PI-inorganic hybrids affords flexibility to the brittle hybrids. PDMS has been introduced into PI as copolymers in a form of poly(imide-siloxane) that shows many properties such as flexibility, high gas permeability, low water absorption, modified surface properties, adhesive properties and improved flame resistance [3]. But the introduction of PDMS in the form of copolymer as poly(imide-siloxane) lowers physical and thermal properties of PI.

So far, no study has been reported on PI-PDMS hybrid by blending PDMS into PI via the sol-gel reaction of diethoxydimethylsilane (DEDMS) in poly(amide acid) (PAA), followed by thermal imidization. In our previous research, we introduced PDMS into PI-clay nanocomposites to overcome the brittle behavior of the nanocomposites [4]. In the current study, we investigated the effect of the in-situ formed PDMS on the mechanical and thermal properties of PI. PI-silica-PDMS hybrids were also made for further improving the properties of PI.

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## 2. EXPERIMENTAL

### 2.1. Reagents

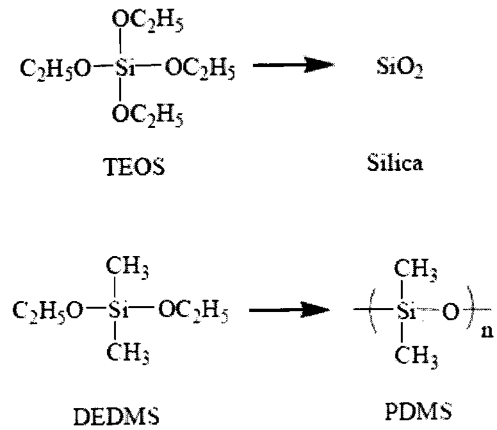
3, 3', 4, 4'-biphenyltetracarboxylic dianhydride (BPDA) and p-phenylenediamine (PDA) were purified by sublimation. PAA was prepared from BPDA and PDA. DEDMS and TEOS were used as received.

### 2.2. Preparation of PI-PDMS hybrids

A mixture of PAA, required amount of DEDMS ( for 1, 3, 5, 10% PDMS), and water was stirred for 24 h, cast on glass plates, dried in vaccume oven at 60°C for 16 h, and then cured stepwise up to 350°C.

### 2.3. Preparation of PI-silica-PDMS hybrids

A mixture of PAA, TEOS and water was stirred for half an hour at room temperature to give a transparent yellow viscous solution. Required amount of DEDMS (for 5% PDMS) and water (double mmol of PDMS) was added into the solution and then stirred for 24 h. The blends were cast on glass plates, dried in vaccume oven at 60°C for 16 h, and then cured stepwise up to 350°C.




Scheme 1. Preparation of silica and PDMS through sol-gel process

## 3. RESULTS & DISCUSSIONS

### 3.1. Preparation of hybrid films

PI-silica and PI-PDMS hybrids were prepared from PI and different ratio of inorganics (1, 3, 5, 10%). In the case of PI-silica hybrids, silanol groups are formed from TEOS in the presence of water, and the silanol reacts each other to form silica. Silanol groups are also formed from DEDMS in the presence of water by hydrolysis and these silanols provide PDMS (1, 3, 5, 10%) by reacting each other in the case of PI-PDMS hybrids (Scheme1). PI-silica-PDMS hybrids were prepared by introducing PDMS (1, 3, 5, 10%) in where silica content were fixed to 5%. Furthermore, PI-silica-PDMS hybrids were made by introducing silica (1, 3, 5, 10%) in where PDMS content were fixed at 5%.

Imidization was followed by IR. In the case of PI-silica-PDMS hybrids, the characteristic absorption peaks of imide groups at 1774 $cm^{-1}$ (C=O symmetric stretching), 1718 $cm^{-1}$ (C=O asymmetric stretching), and 1361 $cm^{-1}$ (C=N stretching) were observed after 300°C curing. The siloxane stretching band was observed at 1000• •1100 $cm^{-1}$. Other characteristics absorptions were also observed at 835 $cm^{-1}$ associated with methyl-silane, and at 1517 $cm^{-1}$ associated with aromatic C=C bond.

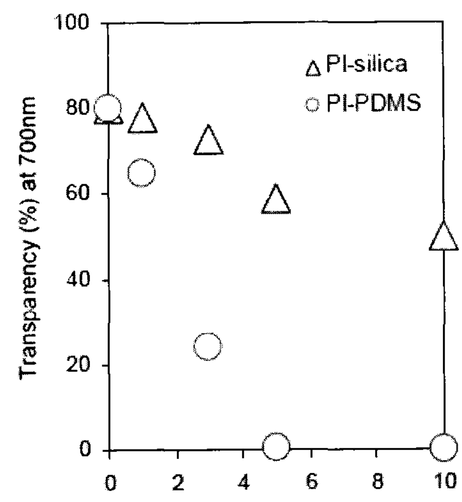



Fig.1. Transparency of PI-silica and PI-PDMS hybrids

### 3.2. Morphology of hybrids

Transparency of the hybrid films was checked by UV-vis spectrophotometer. The transparency at 700 nm was reduced after inclusion of both silica and PDMS (Fig.1). The transparency was affected by the inorganic particle size and their aggregation.

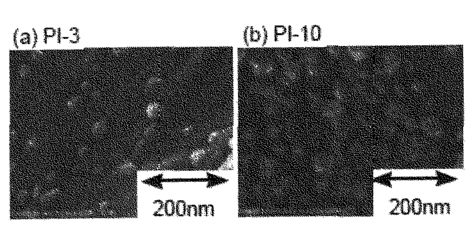



Fig.2. SEM images of PI-PDMS hybrids

The PDMS particles in PI-PDMS hybrids were observed by SEM. PDMS particle size was 20-40nm at 3% PDMS (Fig.2a) which became up to 100nm at 10% PDMS (Fig.2b). The circular smaller size of PDMS made the hybrids with 1 - 3% PDMS transparent, but the hybrids with 5 - 10% PDMS became opaque because of aggregation of inorganics.

In the case of PI-silica-PDMS hybrids, the particles were circular in shape and size was about 30-40nm, which makes the hybrid films transparent when silica and PDMS contents were 1 to 5% (Fig.3a and c). Hybrid films with 10% silica (Fig.3b) and 10% PDMS (Fig.3d) became darker. The hybrid of PI - 5% PDMS was opaque. Interestingly, however, hybrid became transparent when 1 to 5% silica was further added into it. It happened because of the sharing of silanol groups of TEOS and DEDMS between each other and fine distribution of inorganics.

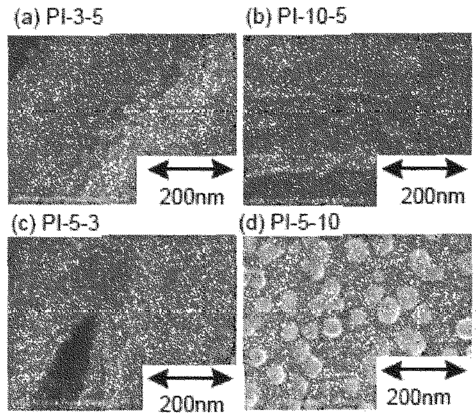



Fig.3. SEM images of PI-silica-PDMS hybrids

### 3.3. Tensile properties of PI-hybrids

The tensile properties of PI-PDMS, PI-silica and PI-silica-PDMS hybrid films were examined by stress-strain tests (Table 1). In the case of PI-silica hybrids, tensile modulus increased with increasing of silica content but tensile strength and elongation at break decreased with increasing of silica contents. The pronounced increase in the tensile modulus comes from the dispersion of the rigid silica particles into PI film.

In the case of PI-PDMS hybrids, toughening effect of PDMS increased the tensile properties. Small amount of PDMS (1 - 3%) increased the tensile modulus, strength and elongation nicely. But tensile properties decreased with higher PDMS contents (above 5%) due to aggregation.

In the case of PI-silica-PDMS hybrids, small amounts of silica and PDMS remarkably increased tensile modulus, tensile strength and elongation at break from the pristine PI because of the toughening effect of PDMS, rigidity of silica and fine distribution of inorganics. Reduction of tensile properties was found after adding higher PDMS and silica contents due to the aggregation of inorganics.

Table 1. Tensile properties of PI and PI- hybrids

| Type of PI (PI-silica%-PDMS%) | Modulus (GPa) | Strength (MPa) | Elongation (%) |
|---|---|---|---|
| PI | 8.2 | 340 | 30 |
| PI-1-0 | 9.5 | 360 | 25 |
| PI-3-0 | 10 | 300 | 20 |
| PI-5-0 | 11 | 280 | 15 |
| PI-10-0 | 11.5 | 210 | 10 |
| PI-0-1 | 8.5 | 360 | 35 |
| PI-0-3 | 8.8 | 380 | 40 |
| PI-0-5 | 7.5 | 300 | 25 |
| PI-0-10 | 6.5 | 280 | 15 |
| PI-1-5 | 7.5 | 300 | 35 |
| PI-3-5 | 9.5 | 400 | 40 |
| PI-5-5 | 10 | 380 | 25 |
| PI-10-5 | 11 | 330 | 20 |
| PI-5-1 | 11 | 360 | 30 |
| PI-5-3 | 10.5 | 410 | 35 |
| PI-5-5 | 10 | 380 | 25 |
| PI-5-10 | 8 | 320 | 20 |

BPDA-PDA

### 3.4. DMA of PI hybrids

DMA of the hybrid films were carried out to investigate the effect of silica and PDMS on the thermomechanical properties of the PI hybrid films. The $T_g$ of the pristine PI was 311 and 320°C from the loss modulus (E") and tanδ, respectively. In the case of PI-silica hybrids, presence of silica increased the $T_g$ (Table 2). In the PI-PDMS hybrids, the presence of PDMS whose $T_g$ is about -125°C arose lower $T_g$ (Table 2). Surprisingly, in the PI-PDMS hybrids, $T_g$ based on PI was higher than the pristine PI.

In the PI-silica-PDMS hybrids, presence of silica (1-10%) and PDMS (1-10%) increased $T_g$ than the pristine PI (Table 2). In the hybrids, lower $T_g$ arose due to the presence of PDMS. Small content of silica (1-5%) and PDMS (1-5%) increased $T_g$ prominently. But higher inorganic contents (10%) decreased $T_g$ due to aggregation. The $T_g$ is considered to be affected by molecular packing, chain rigidity, linearity and above all molecular motion. The increase of $T_g$s after adding of inorganics can be attributed to the nanometer size of inorganics which restricts segmental motion near the organic-inorganic interface.

Table 2. $T_g$ of various PIs

| Type of PI (PI-silica%-PDMS%) | Lower $T_g$ (°C) | | Higher $T_g$ (°C) | |
|---|---|---|---|---|
| | E'' | tanδ | E'' | tanδ |
| PI | --- | --- | 311 | 320 |
| PI-1-0 | --- | --- | 337 | 361 |
| PI-3-0 | --- | --- | 333 | 357 |
| PI-5-0 | --- | --- | 330 | 351 |
| PI-10-0 | --- | --- | 312 | 320 |
| PI-0-1 | -17 | -33 | 328 | 366 |
| PI-0-3 | -30 | -35 | 331 | 371 |
| PI-0-5 | -39 | -38 | 333 | 368 |
| PI-0-10 | -59 | -59 | 316 | 330 |
| PI-1-5 | -44 | -39 | 328 | 366 |
| PI-3-5 | -56 | -50 | 331 | 371 |
| PI-5-5 | -57 | -57 | 333 | 368 |
| PI-10-5 | -51 | -69 | 316 | 330 |
| PI-5-1 | -50 | -34 | 318 | 352 |
| PI-5-3 | -54 | -44 | 346 | 386 |
| PI-5-5 | -57 | -57 | 315 | 344 |
| PI-5-10 | -77 | -87 | 315 | 333 |

### 3.5. Thermal stability of PI hybrids

The thermal stabilities of PI and their hybrids were studied by TGA in argon. The 5 and 10% weight loss temperatures ($T_5$ and $T_{10}$) and weight residue at 800°C of the PI-silica and PI-PDMS hybrids with 1 to 10% silica and PDMS showed higher thermal behavior in all respects than the pristine PI.

In the case of PI-silica-PDMS hybrids, at constant PDMS content (5%), inclusion of higher silica contents increased $T_5$ and $T_{10}$ than the pristine PI (Fig.4). For example, $T_5$, $T_{10}$ and weight residue at 800°C of the pristine PI were 563°C, 583°C, and 60.8%, which became 581°C, 594°C and 69.4% in the case of PI-10-5 hybrid. When the silica content was fixed at 5%, inclusion of more PDMS decreased $T_5$ and $T_{10}$ but still higher than the pristine PI and weight residue at 800°C was increased. In the case of PI-5-1 hybrid, $T_5$ and $T_{10}$ were 576°C and 590°C, which became 565°C and 584°C in the case of PI-5-10 hybrid. The thermal properties of silica and PDMS are high, which also enhanced the thermal behavior of the hybrids.

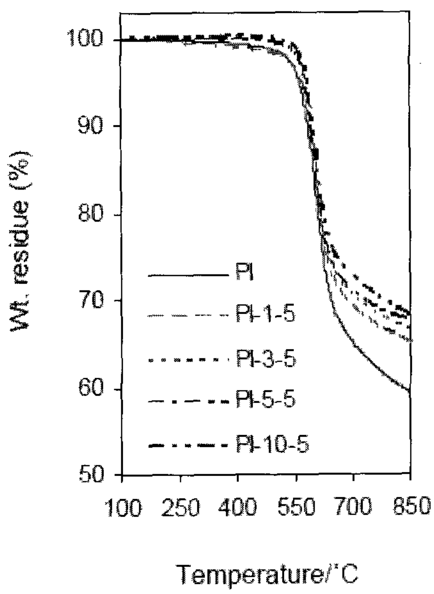



Fig.4. Effect of silica on TGA of PI-silica-PDMS hybrids

## 4. CONCLUSIONS

Novel organic-inorganic hybrids of PI-PDMS, PI-silica, and PI-silica-PDMS were prepared through in-situ sol-gel process. PI-silica hybrid provided higher thermal performance but brittle behavior. PI-PDMS hybrids increased thermal and mechanical properties with opaqueness. PI-silica-PDMS hybrids provided excellent thermal and mechanical performance with transparency in the presence of suitable contents of silica (3 - 5%) and PDMS (3 - 5%). In-situ sol-gel process was thus shown to be a successive way for the preparation of PI-inorganic hybrids.

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