Novel Organic-Inorganic Hybrids from Polyimide Using Sol-gel Method

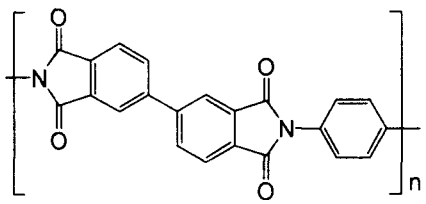
Shaikh Md. Mominul Alam, Takehiro Kawauchi and Tsutomu Takeichi

School of Materials Science, Toyohashi University of Technology,
Tempaku-cho, Toyohashi 441-8580, Japan.
Tel.: +81(0)532 44 6815; Fax: +81(0)532 48 5833; Email: takeichi@tutms.tut.ac.jp

1. Introduction

Aromatic polyimides (PI) exhibits outstanding thermomechanical, dielectrical properties and now is extensively used in various sectors like microelectronics, aerospace, 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 matrics increase the thermal stability, gas barrier property, flame resistance and corrosion protection but decrease the elongation and toughness [1]. PI-silica binary hybrid is another approach to promote the properties of PI. PI and silica from metal alkoxide by sol-gel processs provide hybrid which has improved mechanical and thermal properties but the film become brittle [2]. The current study is an effort to overcome the brittle problem of PI-silica hybrid.

It is expected that introduction of polydimethylsiloxane (PDMS) into PI-inorganic hybrids affords flexibility to the brittle PI-inorganic. One approach is to introduce PDMS by copolymerization. Introduction of PDMS groups in a form of poly(imide-siloxane) show many properties such as flexibility, high gas permeability, low water absorption, modified surface properties, and adhesive properties. But the introduction of PDMS in the form of block copolymer as poly(imide-siloxane) lowers thermal properties and mechanical performance like tensile modulus [3, 4]. Another approach to introduce PDMS is in-situ sol-gel reaction of diethoxydimethylsilane (DEDMS) in a polymer matrix. Previously, we succeeded in toughening the brittle PI-clay hybrid by introducing PDMS through the sol-gel reaction of DEDMS [5]. The hybrid was prepared by the sol-gel reaction in the presence of clay and poly(amide acid) (PAA) as the precursor of PI. In this study, we applied the versatile methodology to toughen brittle PI-silica hybrids. The effect of in-situ formed PDMS on the mechanical and thermal properties were investigated. PI-silica and PI-PDMS hybrids were also made for comparison. In this study, PI prepared from 3, 3′, 4, 4′-biphenyltetracarboxylic dianhydride (BPDA) and *p*-phenylenediamine (PDA) was used (Scheme 1).



Scheme 1. Structure of **PI (BPDA/PDA)**

2. Experiment

2.1. Preparation of PI-Silica and PI-PDMS hybrids

PI-silica or PI-PDMS binary hybrids were prepared from PAA and TEOS or DEDMS as following way: Into a flask equipped with mechanical stirrer, certain amount of PAA was stirred with required amount of TEOS or DEDMS and double mmol of water for 24 h at room temperature. All the blends were cast on glass plates, dried in a vaccume oven at 60°C for 16 h and then cured at 100, 200, 300°C 1 hr each and then 350°C for 15min each to obtain hybrid films.

2.2. Preparation of PI-silica-PDMS hybrids

The PI-silica-PDMS hybrids were prepared from PAA, TEOS and DEDMS as following way: Into a flask certain amount of PAA and TEOS and double mmol of water were placed. The reaction mixture was

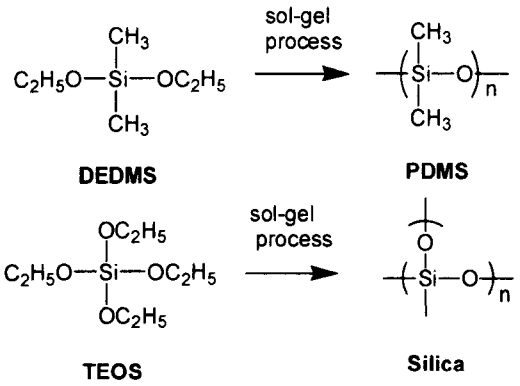
stirred for half an hour at room temperature to give a transparent yellow viscous solution. Required amount of DEDMS and water was added into the solution and then stirred for 24 h. All the blends were cast on glass plates, dried in a vaccume oven at 60°C for 16 h and then cured stepwise up to 350°C to obtain yellow films. The hybrids were addressed PI-silica%-PDMS% at this order in this research. As an example, PI-3-5 corresponds to a hybrid containing 92% PI, 3% silica and 5% PDMS.

3. Results and Discussion

3.1. Preparation of hybrid films

PI-silica and PI-PDMS binary hybrids were prepared from PI and different ratio of inorganics. Silica and PDMS were introduced by sol-gel process (Scheme 2). PI-silica-PDMS hybrids were prepared by introducing PDMS and silica at various contents.

Imidization was followed by IR. In 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 rang from 1000 to 1100 cm^{-1}. Other characteristics absorptions were also observed at 835 cm^{-1} associated with c(methyl)-Si, at 1517 cm^{-1} associated with aromatic C=C bond. From IR, it can be concluded that the hybrid is PI-silica-PDMS hybrid after curing.



Scheme 2. Preparation of **PDMS** and **Silica** through sol-gel process

3.2. Morphological study

Transparency were checked by UV-vis spectrophotometer. At 700nm wave length, transparency of pristine PI was 76%. As shown in Fig.1 (a) and (b), the transparency decreased after inclusion of silica and PDMS.

The particle size of inorganics in PI was observed by SEM (Fig.2). In case of PI-silica hybrids, silica size became 30-60nm at 10% silica. The relatively small size of silica made all PI-silica hybrids transparent. But in case of PI-PDMS hybrids, less than 3% PDMS related hybrids are transparent but more than 5 % PDMS made the hybrid opaque because of the bigger size and aggregation of inorganics.

The transparency for PI-PDMS (5%) hybrid was 7.6%, and particle size was 40-100nm. However, by introducing 3% silica into the hybrid, transparency became 56% and particle size 20-40nm (Fig. 1 & 2).

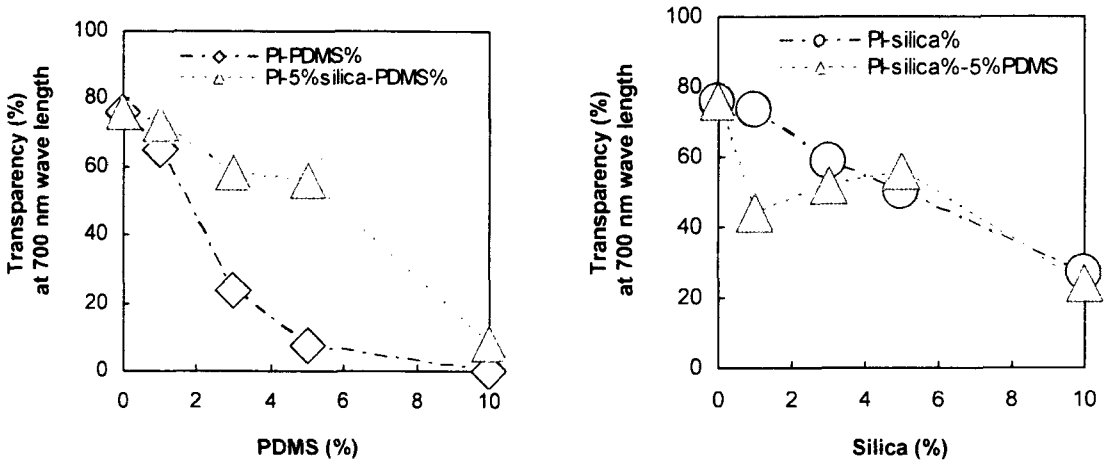


Fig.1. Transparency (%) of PI-hybrids by the inclusion of **PDMS** (a) and **silica** (b)

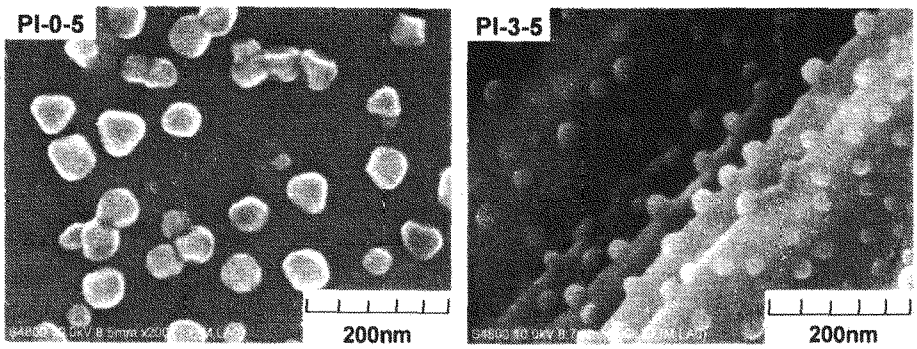


Fig.2. SEM-images of PI-0-5 and PI-3-5 hybrids

3.3. Tensile properties of PI-hybrids

The tensile properties of PI-PDMS, PI-silica and PI-silica-PDMS hybrid films were examined and the results are summarized in Table 1. For pristine PI, tensile modulus, tensile strength and elongation at break were 8.1 GPa, 344MPa and 31%, respectively. PI-silica hybrids had increased tensile modulus but decreased tensile strength and elongation. The pronounced increase in the tensile modulus comes from the dispersion of the rigid silica particles into PI film.

In case of PI-PDMS hybrids, small amount of PDMS (up to 3%), increased tensile performance nicely due to the toughening effect of PDMS.

In case of PI-3-5 and PI-5-3 hybrids, small amount of silica and PDMS increased the tensile modulus, tensile strength, elongation at break than pristine PI (Table 1 & Fig.3).

Table 1. Tensile properties of various PI-hybrids

Type of PI (PI-silica%-PDMS%)	Modulus (GPa)	Strength (MPa)	Elongation (%)
PI	8.1	344	31
PI-1-0	9.4	371	27
PI-3-0	10.0	308	22
PI-5-0	10.9	281	17
PI-10-0	11.2	212	13
PI-0-1	8.5	366	34
PI-0-3	8.6	387	42
PI-0-5	7.5	312	35
PI-0-10	6.7	251	19
PI-1-5	7.6	292	36
PI-3-5	9.4	392	42
PI-5-5	10.0	357	26
PI-10-5	10.9	315	21
PI-5-1	10.9	363	34
PI-5-3	10.4	409	36
PI-5-5	10.0	357	26
PI-5-10	7.8	316	21

3.4. DMA of PI hybrids

DMA for the hybrid films were carried out to see the effect of silica and PDMS on the thermomechanical properties of the PI films. The T_g of pristine PI was 320°C from tanδ. For the PI-silica hybrids, T_g from tanδ became 361, 357, 351, 320°C after inclusion of 1, 3, 5 and 10% silica. For the PI-PDMS hybrids, T_g from tanδ became 366, 371, 368, 330°C after inclusion of 1, 3, 5 and 10% PDMS. Small amount of silica and PDMS (up to 5%) increased the T_g than the pristine

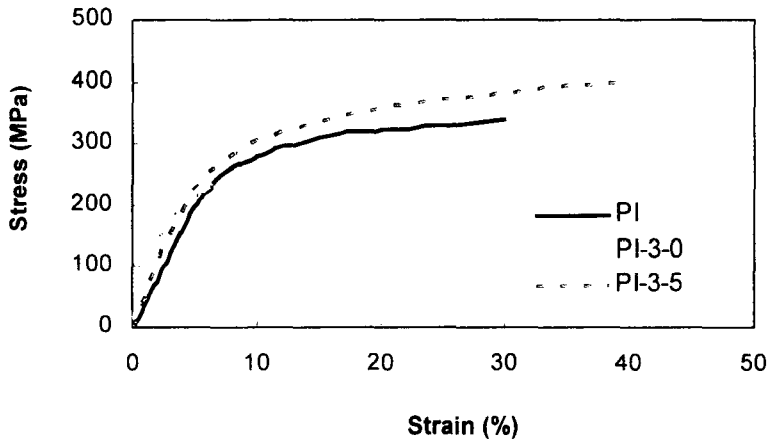


Fig.3. Tensile properties of PI, PI-3-0 and PI-3-5 hybrids

PI. The T_gs related to different PI-silica-PDMS hybrids are summarized in Table 2. The lower T_g decreased by increasing PDMS. The higher T_g of the PI-silica-PDMS hybrids showed even higher T_gs than the T_g for the pristine PI in where small amount of silica and PDMS (1-5%) increased the T_gs prominently. The T_g is considered to be affected by molecular packing, chain rigidity, linearity and above all molecular motion. The increase of T_gs after adding of inorganics can be attributed to the nanometer size of inorganics which restricts segmental motion near the organic-inorganic interface. Moreover, interfacial interaction like hydrogen bonding between PI and inorganic phases may be another cause to increase T_gs.

Table 2. T_g of PI-silica-PDMS hybrids

(PI-silica %-PDMS %)	Lower T_g (°C)	Higher T_g (°C)
PI	---	320
PI-1-5	-39	341
PI-3-5	-50	348
PI-5-5	-56	344
PI-10-5	-69	333
PI-5-1	-34	352
PI-5-3	-44	386
PI-5-5	-57	344
PI-5-10	-87	333

3.5. Thermal stability of PI hybrids

The thermal stabilities of PI and their hybrids in argon were studied by TGA. The 5% degradation temperature (T_5), 10% degradation temperature (T_{10}) and wt. residue% at 800°C of the PI-silica and PI-PDMS hybrids with 1 to 10% silica or PDMS were higher than PI and proved high thermal behaviour of the hybrids.

For PI-silica-PDMS hybrids with constant PDMS content (5%), inclusion of higher silica contents increased the T_5 and T_{10}. When the silica content fixed at 5%, inclusion of more PDMS increased the T_5, T_{10} and wt. residue% at 800°C, which proved the enhancement of thermal behaviour of the PI-silica-PDMS hybrids.

4. Conclusions

Various novel organic-inorganic hybrids of PI were prepared through in-situ polymerization via sol-gel process. PI-silica hybrids provided higher thermal performance but brittle behaviour. PI-PDMS hybrids increased thermal and mechanical properties with opaqueness. PI-silica-PDMS hybrids provided appreciable thermal and mechanical performance with transparency in the presence of lower contents of silica (less than 5%) and PDMS (less than 5%). In-situ sol-gel process was proved as a successful way for the synthesis of PI-inorganic hybrids.

References

[1]. T. Agag, T. Koga, T. Takeichi, *Polymer*, 42, 3399, 2001.
[2]. H. Wang, W. Zhong, P. Xu, Q. Du, *Macromol. Mater. Eng.*, 289, 793, 2004.
[3]. M. Simionescu, M. Marcu, M. Cazacu, C. Racles, *Europ. Polym. J.*, 38, 229, 2002.
[4]. J. E. McGrath, D. L. Dunson, S. J. Mecham, J. L. Hedrick, Adv. In Polym. Sci., 140, 61, 1999.
[5]. S. M. M. Alam, T. Agag, T. Kawauchi, T. Takeichi, *React. Funct. Polym.*, 67, 1218, 2007.