

Polyimide – Polysiloxane Nanohybrid : Synthesis and Performance

Shaikh Md. Mominul Alam

Bangladesh University of Textiles, Tejgaon, Dhaka-1208, BANGLADESH.

ABSTRACT

A series of polyimide (PI) and polysiloxane (PSX) nano-hybrids were prepared through in-situ sol-gel process of PSX to investigate the functional group and rational effect of PSX in PI-PSX hybrids. PI was prepared from 3, 3', 4, 4'-biphenyltetracarboxylic dianhydride (BPDA), p-phenylenediamine (PDA). PSX like polydimethylsiloxane (PDMS), polymethylphenylsiloxane (PMPS) and polydiphenylsiloxane (PDPS) were prepared by the sol-gel reaction of diethoxydimethylsilane (DEDMS), diethoxymethylphenylsilane (DEMPS) and diethoxydiphenylsilane (DEDPS) accordingly. PI-5%PDMS hybrid provided higher elongation at break% where as PI-5%PDPS hybrid had higher tensile modulus than pristine PI. PI-5%PDPS or PMPS hybrid became more transparent but PI-5%PDMS hybrid became opaque. Weight residue % at 800°C, glass transition temperatures of all hybrids were higher than pristine PI.

Keywords: Polyimide, Polysiloxane, sol-gel reaction, tensile modulus, opaque.

1. Introduction

Polyimides are considered to be one of the super-engineering materials due to their excellent thermal, mechanical and dielectric properties [1] which has been applied it to a wide range of industrial fields, such as microelectronics and aerospace engineering.

Hybridization is an up-date technique to incorporate inorganic materials into polyimide for combining the advantages of organic polymer and inorganic materials [2-4].

Among inorganic materials, PSX are the most common and one of the most important organosilicon polymers used in polymer chemistry[2]. The functional group of polysiloxane can play an important role on their behaviors. PDMS is widely used polysiloxane whose repeating unit is $[-SiO(CH_3)_2-]$ in where two methyl groups are attached as side chain. Another form of PSX is phenyl containing siloxanes. The phenyl group is usually incorporated as PMPS $[-Si(CH_3)(C_6H_5)O-]$ or a PDPS $[-Si(C_6H_5)_2O-]$. Though the main chain of PDMS, PMPS, PDPS is same $(-Si-O-Si-)$ but due to the side functional group their properties are so different among one another (Scheme 1).

The present study is carried out to provide results useful for comparing the properties of among the

hybrids produced from PI and different ratios (5, 10, 20, 50%) of PDMS, PMPS and PDPS. PDMS, PMPS, PDPS were developed into polyamic acid from alkoxy silane like DEDMS, DEMPS and DEDPS respectively through in-situ sol-gel process. The current research interest is to prepare hybrids with PI and those 3 PSX individually to observe the effect in performance of hybrids mainly thermal and mechanical aspects.

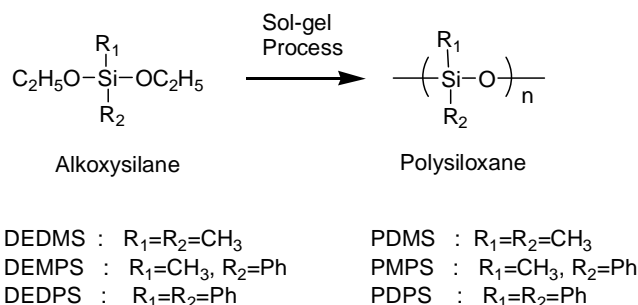
2. Experimental

2.1 Reagents

BPDA and PDA from Tokyo Kasei Kogyo Co. Ltd, Japan were purified by sublimation. N-Methyl-2-Pyrrolidone (NMP) from Osaka Chemicals, Japan was dried by distillation under reduced pressure over Sodium Hydride. DEDMS, DEDPS, DEMPS from Wako Pure Chemical, Japan were used as received. PAA was prepared from BPDA and PDA in NMP (Scheme 2) in where inherent viscosity of the PAA was 2.20 dl/g (0.5g/dl in NMP at 30°C).

2.2 Synthesis of PI

In a three necked flask fitted with a mechanical stirrer, 2.589g (24mm) PDA 86.90ml of NMP was

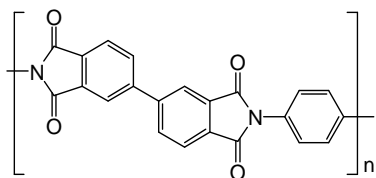


Scheme 1. Synthesis of PSX

* Corresponding author. Tel.: +88-01713171365

E-mail address: dalim70@yahoo.com

stirred until clear solution were got under nitrogen atmosphere. 7.06g (24mm) of BPDA and rest amount of NMP were added and stirring was continued up to 12 hrs at room temperature. The solution was cast onto a glass plate and successive heating at 60°C/16h, 100°C/1h, 200°C/1h, 300°C/1h, 350°C/15 min affording transparent film (Scheme 2).



Scheme 2. Structure of PI (BPDA/PDA)

2.3 Preparation of PI-Silica-PDMS hybrids under Sol-Gel process:

The PI-PDMS hybrids were prepared the following way: Into a flask equipped with mechanical stirrer, certain amount of PAA was stirred with required amount of DEDMS about half an hour. Water (mole ratio of DEDMS and H₂O=1:2) was then added and stirred about 24 hrs. The solution was cast on glass plates, dried in vacuum oven at 60°C/16 h, 100°C/1h, 200°C/1h, and then 300°C/1h, 350°C/15 min. in an air circulating oven to obtain solid films.

PI-PMPS and PI-PDPS hybrids were prepared in the similar way by using DEMPS and DEDPS as PSX, respectively.

2.4 Measurements

IR spectra were obtained with Jasco Spectrophotometer model FT/IR-420. DSC was recorded using Rigaku Thermo Plus 2DSC8230 at a heating rate of 10°C/min under nitrogen. TGA was performed with Rigaku Thermo Plus 2TG-DTA TG8120 at a heating rate of 5°C/min under argon. Dynamic mechanical analysis (DMA) were conducted on ORIENTEC Automatic Dynamic Viscoelastomer Rheovibron model DDV-01FP at 35Hz at a heating rate of 4°C/min. Tensile properties were recorded with Imada Seisaku-sho Model SV-3. SEM from Hitachi S-4800 was used to check the particle size of inorganics.

2.5 IR of PI-PSX hybrids

Imidization and curing of the hybrids were checked by IR. In case of all PI- hybrids, after 350°C curing, the characteristic peak related to absorption of imide group at 1776cm⁻¹ C=O symmetric stretching, 1730cm⁻¹ C=O asymmetric stretching, 1365cm⁻¹ C=N stretching were found which proved the hybrids are PI-hybrids. The absorption peak related to Si-O-Si were seen at 1000-1100 cm⁻¹, which also became larger after adding higher content of inorganics. The Si-OH related pick were found at 1000-1050cm⁻¹, which became smaller after arising curing temperature and proved the

conversion from Si-OH to Si-O-Si. In case of PI-PMPS and PI-PDPS hybrids, the C-H stretching of phenyl group were seen at 3070cm⁻¹ which proved the presence of side functional group in hybrids as well.

2.6 DSC of PI-PSX hybrids

Polymerization were confirmed by DSC. In case of all hybrids endotherm happened due to imidization of PI mainly. After 200°C curing, endotherm disappeared and polymerization may be completed. IR-spectras of the hybrids also shown the characteristics picks related to PI at 200°C curing and supported the DSC results. The amount of endotherm of pristine PI at 100°C curing is about 146.05 J/g. The amount of endotherm at 100°C curing are 78.94, 58.12, 46.2, 31.55 J/g for PI-PDMS hybrids, 126.05, 116.94, 114.58, 77.97 J/g for PI-PMPS hybrids and 142.21, 124.79, 120.18, 63.24 J/g for PI-PDPS hybrids at 5, 10, 20, 50% inorganics. The amount of endotherm of PI-PSX hybrids became lower at higher contents of PSX which proved the addition of inorganics in hybrids at higher ratios. The amount of endotherm related to PI-PDPS, PI-PMPS hybrids are lower than those of PI-PDMS hybrids may be due to higher crystalline in nature of phenyl related PSX. In XRD-results, we have seen no pick in case of PI-PDMS related hybrids. But in case of XRD-results of PI-PDPS hybrids, pick related to the crystalline structure of PDPS have seen. PI-50%PMPS-hybrids also showed slight pick in XRD.

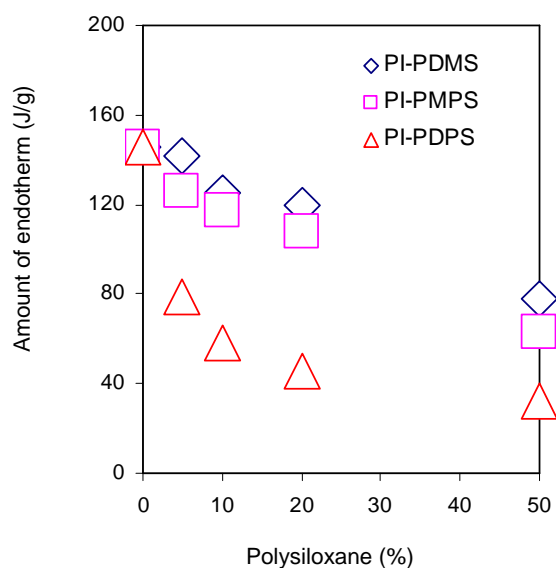


Fig 1. Amount of endotherm of PI-PSX hybrids

2.7 Transparency of PI-PSX hybrids

The transparency of the hybrids were checked by UV-spectrophotometer and results are plotted in Fig. 2. Pristine PI transparency is about 76% at 700nm wave no. The transparency reduced tremendously like 7.6, 1.4, .016, .014% after adding 5, 10, 20, 50% PDMS. But when introduced 5, 10, 20, 50% PDPS, the transparency became 82, 77, 76, 60%. The transparency

became 80, 72, 9, 0.4% after adding various ratio (5, 10, 20, 50%) of PMPS. It is well known that aromatic PI with coloration of pale yellow to deep brown strongly absorb visible light because of their aromatic conjugated structure and the intermolecular and intra molecular charge transfer complexes (CTCs) formed between and within Polymer chain. Phenyl-phenyl (PI-PDPS) interaction increase compatibility between two phases. Small PDPS and PMPS domain affect the electron state of PI and hinder to develop intermolecular CTCs and increase transparency. The higher contents of polysiloxane reduced transparency due to the aggregation of inorganics.

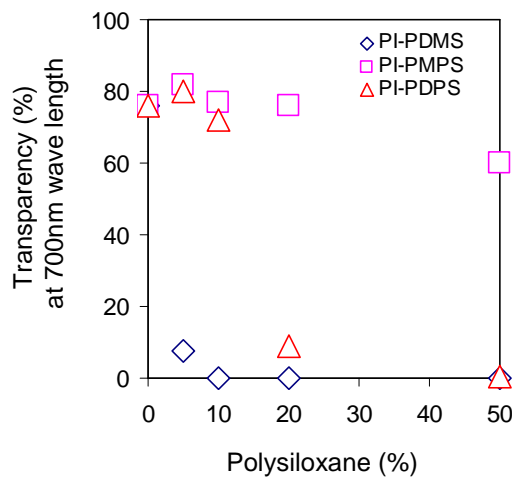


Fig 2. Transparency of PI-PSX hybrids

2.8 Morphological study

The shape and size of inorganics in various PI-hybrids were seen by SEM. SEM-images were taken both from fracture surface and etching system. In PI-PDMS hybrids, the inorganic particle size were about 30-60 nm in case of PI-5%PDMS hybrids. The particle became aggregated at high contents (10-50%). The PDPS and PMPS particles sizes were about 30-50nm at low content (5 and 10%) PSX related PI-hybrids. In case of high content of PI-PDPS (20, 50%) hybrids, the particles became aggregated but the aggregation is not as severe as PI-PMPS (20, 50%), PI-PDMS (20, 50%) hybrids. From above discussion, it can conclude that the tendency of self condensation of methyl related PSX is much more higher than phenyl-related PSX may be due to π - π interaction between PI and Phenyl functional group of PSX. High condensation rate produced bigger particle also aggregation in case of PI-PDMS related hybrids. The aggregation of PDMS and high (20, 50%) content PMPS made the hybrids opaque.

3. Properties of PI-Silica-PDMS films

3.1 Tensile properties

The mechanical properties of PI and PI-PSX hybrids were examined and the results are summarized

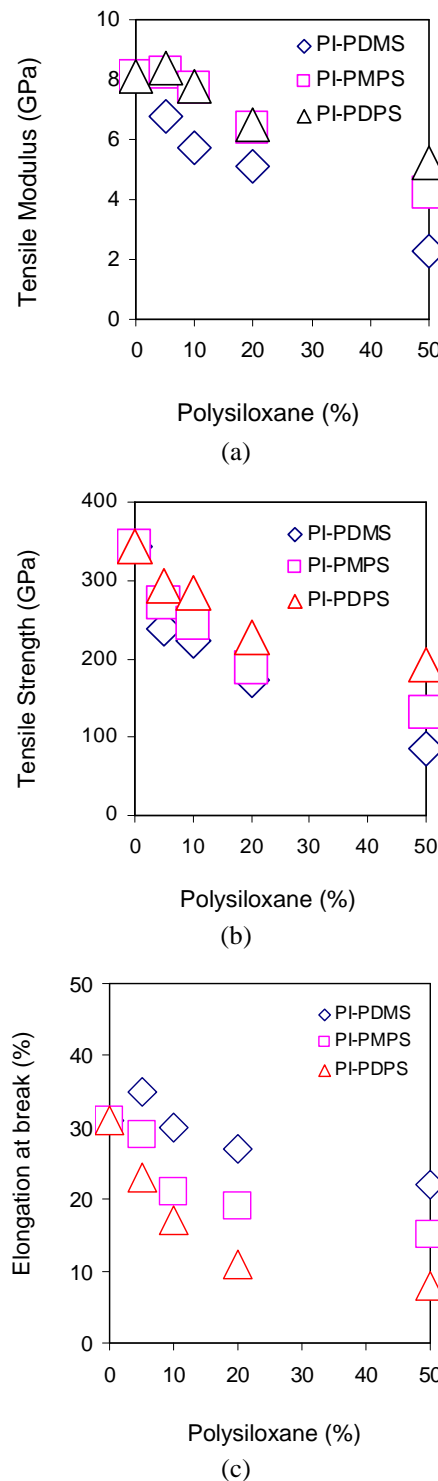


Fig 3. Effect of Polysiloxane (%) on (a)Tensile modulus (b)Tensile strength (c) Elongation at break% of PI-Polysiloxane hybrids

in Fig 3. In comparison of pure PI, the PI-5%PDMS hybrid decreased the modulus and the tensile strength while the elongation at break increased upon incorporating PDMS as a flexible particle into the

matrix. Due to the poor interfacial interaction between PI and PDMS particles and the incorporation of large PDMS particles with aggregation of inorganics lead to the inferior mechanical properties. In case of PI-PDPS and PI-PMPS hybrids, the modulus of PI-5 hybrids increased nicely than pristine PI due to the rigidity of side aromatic functional group and π - π interaction between PI and inorganics. Though the strength of PI-PSX hybrids were lower than pristine PI but it can be carefully observed that the hybrids related to phenolic side function groups (PI-PDPS, PI-PMPS) showed higher tensile strength due to π - π interaction than PI-PDMS hybrids. The high crystal behavior of phenolic group related PSX decreased the elongation at break% of the PI-PDPS and PI-PMPS hybrids.

3.2 Dynamic mechanical properties

DMA was done mainly to observe the glass transition temperatures of the hybrids [Fig 4]. All PI-PSX hybrids showed two T_g s---- the lower T_g is for PSX and the higher T_g is for PI. The tendency of the lower T_g s always tends to the T_g of related PSX after increasing the ratio. As example, PDMS T_g is about -120°C. The lower T_g of PI-PDMS hybrids tends to the T_g of PDMS after increasing the contents of PDMS into the hybrids. So PI-PDMS hybrids T_g decreased from -39.4°C to -68.7 after inclusion of 5 to 50% PDMS. Also PDPS T_g is about 49°C. So the lower T_g of PI-PDPS hybrids became -33.7 to 44.2°C after inclusion 5 to 50% PDPS into PI. The lower T_g of PI-PMPS hybrids showed the same phenomena.

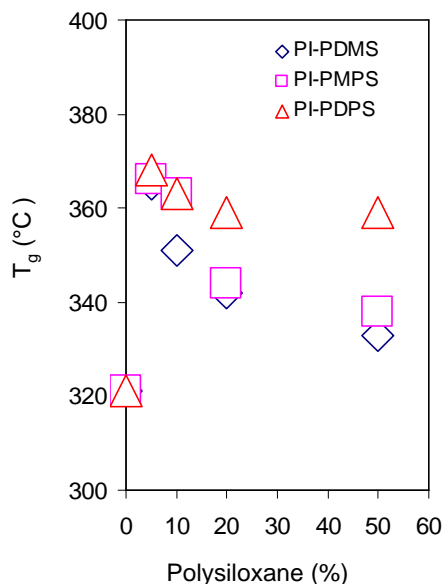


Fig 4. DMA of PI-PSX hybrids

The higher T_g s of PI-PSX hybrids are higher than the pristine PI (320°C from $\tan\delta$). This happened due to the nanometer size of inorganics which restrict the movement of PI. Also π - π interaction and H-bonding between PI and polysiloxane can provide interfacial

interaction which restrict the segmental motion between phases. The loss modulus of PI-PSX hybrids decreased due to the flexibility of PSX. But Phenyl side functional group related PI-PSX hybrids showed higher modulus than PI-PDMS hybrids which proved the π - π interaction between PI, PSX phases. Even PI-5%PDPS hybrids showed higher modulus than pristine PI at 30°C.

3.3 Thermal properties

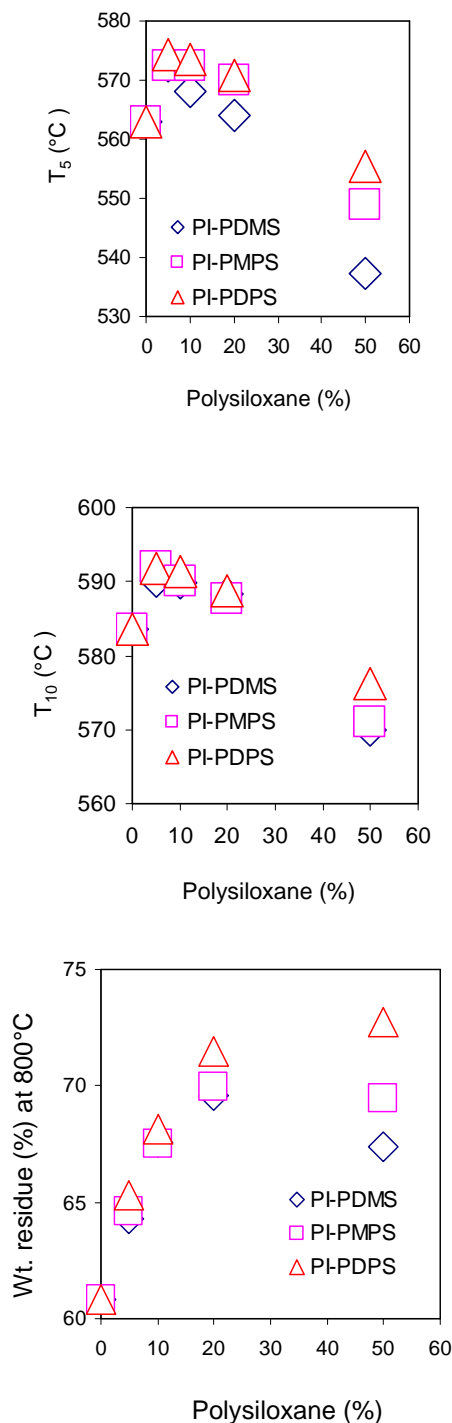


Fig 5. TGA of PI-PSX hybrids

Silicone resin possesses excellent thermal stability because of its special structure, such as high bond energy (443.7 KJ/mol) and high ionic character (about 51%) of Si-O bonds. PDMS is the most common member of the family, and many studies of its thermal properties have been reported. The incorporation of phenyl siloxane in PDMS has been shown to increase its thermal-oxidative stability. Both the onset temperature of thermal degradation and residue content of PDMS containing phenyl groups showed a neat, direct correlation between increasing phenyl content and final weight of residue. The introduction of small amount of MPS or DPS into a PDMS skeleton can increase the onset temperature from 340°C to 400°C. In case of our PI-PSX hybrids, TGA under argon was done to check the thermal stability of PI-PSX hybrids [Fig 5]. PDPS, PMPS related hybrids showed higher 5% degradation temperature (T_5), 10% degradation temperature (T_{10}) and weight residue% at 800°C than PDMS related hybrids. It also noticed that small contents of PSX increased the thermal stability of the hybrids due to the presence of PSX in to PI matrix which hinder the permeability of volatile degradation products out from the material. High contents of PSX made aggregation which degraded thermal stability of the hybrids.

4. Conclusions

PI-PSX hybrids were prepared by PI and various ratio of PSX. Side functional groups showed pronounce influence in transparency, thermal and mechanical properties of the hybrids. The ratio of PSX also can play roll effectively in performance of the hybrids. In-situ sol-gel process can provide PI-PSX hybrids successfully.

REFERENCES

1. K.L Mittal, *Polyimides: Synthesis, Characterization and Application*, Vol.1, Plenum Press, New York and London, (1984).
2. S. M. M Alam, Preparation of Polyimide-Clay Nanocomposites and Their Performance, *Journal of Scientific Research*, Vol.1(2),pp326-333(2009).
3. S. M. M Alam et al., Preparation and Properties of Polyimide-Clay Hybrids Containing In-situ Formed Polydimethylsiloxane, *J. Photopolymer Sci. and Tech.*, Vol.19(2), pp293-296(2006).
4. S. M. M Alam et al., Organic-Inorganic hybrids containing polyimide, organically modified clay and in situ formed polydimethylsiloxane, *React. Funct. Polym.*, Vol.67: pp1218-1224(2007).
5. N. Furukawa et al., Surface and Morphological Characterization of Polysiloxane-Block-Polyimide, *J. Polym. Sci. A: Polym Chem.*, Vol. 35, pp2239-2251 (1997).
6. J.E. McGrath, D.L.Dunsion, S. J. Mecham, and , J.L Hedrick, Synthesis and Characterization of Segmented Polyimide-Polyorganosiloxane Copolymers, *Advances in Polymer Science*, Vol.140, pp61-105(1999)..
7. Y. Yamada, Siloxane modified polyimide for microelectronics coating applications, *High Perform. Polym.*, Vol.10, pp 69-80(1997).
8. P. Sysel, R. Hobzova, V. Sindelar, J. Brus, Preparation and characterization of cross-linked polyimide-poly(dimethylsiloxane)s, *Polymer*, Vol.42, pp10079 -10085(2001).