

SYNTHESIS OF NANO-HYBRIDS FROM POLYIMIDE AND IN-SITU FORMED POLYSILOXANES AND PERFORMANCES

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ABSTRACT

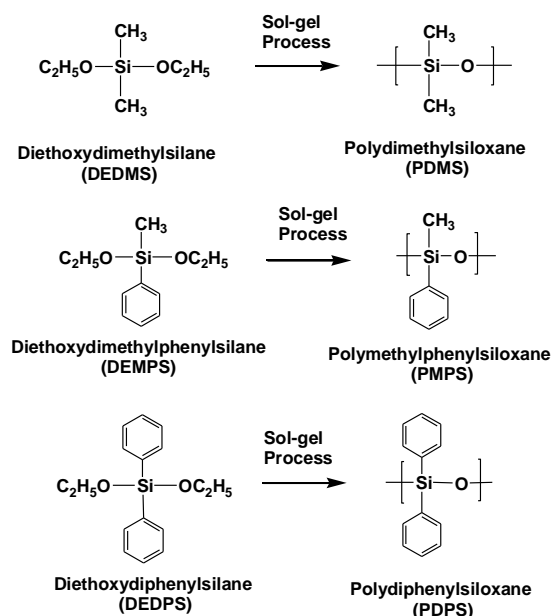
A series of polyimide (PI)-polysiloxane (PSX) hybrids were synthesized and morphology, thermal-mechanical properties were reported. Hybrid solution were obtained through the formulation on different weight ratios (5, 10, 20, 50%) of polysiloxane (PSX) like polydimethylsilane (PDMS), polymethylphenylsilane (PMPS), and polydiphenylsilane (PDPS) in to polyamide acid (PAA). PI and small content (5%) of phenyl related PSX hybrid films increased transparency than pristine PI where as PI-5%PDMS related hybrid film became opaque. Through SEM-images it was observed that inorganic particles separately distributed and sizes were about 10 to 75 nm in PI-5% PMPS, PDPS films where as the particle were about 15 to 100nm and aggregated in case of PI-5%PDMS hybrid film. The % elongation at break of PI-5%PDMS hybrid was higher but 5%PMPS, PDPS reduced the % elongation at break than that of pristine PI. The tensile modulus of PI-5%PDPS, PMPS related hybrids were higher where as PI-5%PDMS related hybrid showed lower tensile modulus than pristine PI. DMA of the PI-PSX hybrids revealed two glass transition temperatures (T_g) corresponding to PSX and PI components. T_g , weight residue % at 800°C of all PI-PSX hybrids were higher than that of pristine PI.

Keywords: Polyimide, Polysiloxane, Hybrid.

1. INTRODUCTION

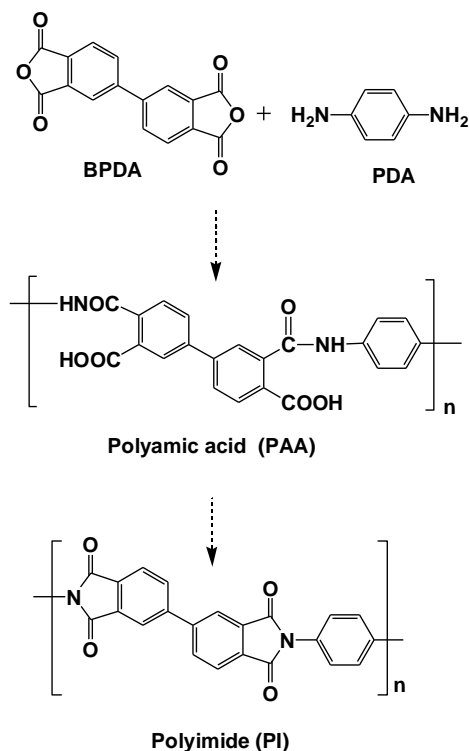
PIs are considered to be one of the super-engineering materials due to their excellent thermal, mechanical and dielectric properties [1] which have been applied to a wide range of industrial fields, such as microelectronics and aerospace engineering. Hybridization is an up-date technique to incorporate inorganic materials into polymer for combining the advantages of organic polymer and inorganic materials [2-3].

Among inorganic materials, PSX are the most common and one of the most important organosilicon polymers (Scheme 1). The backbone of PSX is Si-O-Si but the side functional groups can differ from silane to silane. The functional group of polysiloxane can play an important role on their behaviors. PDMS is widely used polysiloxane in lithographic applications for electronics whose repeating unit is $[-SiO(CH_3)_2-]$ where two methyl groups are attached as side chain. PDMS has excellent thermal and oxidative stability, low absorption in UV, and good oxygen reactive ions etch resistance [4]. Another form of polysiloxane is phenyl containing siloxanes. The phenyl group is usually incorporated as



Scheme 1. Synthesis of Polysiloxanes by in-situ sol-gel process

diphenylsiloxane $[-\text{Si}(\text{C}_6\text{H}_5)_2\text{O}-]$ or a phenylmethylsiloxane $[-\text{Si}(\text{CH}_3)(\text{C}_6\text{H}_5)\text{O}-]$. PDMS has unique thermal and mechanical properties due to its inorganic backbone and its phenolic side chain. PDPS is highly crystalline and forms a mesophase which is intermediate between the crystalline and liquid phases above its melting temperature [5]. PMPS is another important polysiloxane elastomer which is stereochemically irregular (atactic) and therefore noncrystallizable [6]. Though the main chain of PDMS,



Scheme 2. Synthesis of PI (BPDA/PDA)

PMPS and PDPS is same but due to the side functional group their properties are different among one another.

The current research interest is to prepare hybrids with PI and those three type of PSXs individually to observe the effect in performance of hybrids mainly thermal and mechanical aspects. The present study is carried out to provide results useful for comparing the properties among the hybrids produced from PI and different weight ratios (5%, 10%, 20%, 50%) of PDMS, PDPS and PMPS. PDMS, PMPS, PDPS were developed into PAA from DEDMS, DEMPS and DEDPS through in-situ sol-gel process. Sol-gel process is a familiar and reliable technique to develop inorganic network into organic polymer following hydrolysis of alkoxysilane and polycondensation of the hydrolysis products. Hybrid materials can be easily prepared by using sol-gel process in which micro and macrostructure of the hybrids can be controlled by the optimization of the synthetic parameters [7].

2. EXPERIMENTAL

2.1 Materials

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

2.2 Characterization

Size exclusion chromatography (SEC) was measured with JASCO instrument with refractive index detection. THF was used as a carrier solvent at a flow rate of 1.0 ml/min at 40°C. Two polystyrene gel columns (Shodex KF806LX2) were used. A calibration curve was made with PMMA standard to determine molecular weight distribution. IR spectra were obtained with Jasco Spectrophotometer model FT/IR-420. Differential scanning calorimetry (DSC) was conducted using Rigaku Thermo Plus 2DSC8230 at a heating rate of 10°C/min under nitrogen. Transparency of hybrids was checked by JASCO V-550 UV/vis spectrophotometer where all samples thickness were about 30 μm . Scanning electron microscopy (SEM) studies were performed to observe the particle size of inorganics using a Hitachi S-4800 scanning electron microscope with the accelerating voltage of 10 kV and emission current of 10 microampere. Both the film surface were etched by aqueous 1N NaOH and then sputter-coating with Pt-Pd under an electric current of 15 miliampere at 6 Pa for 60s. Tensile properties were recorded from at least 10 tests of each sample with Imada Seisaku-sho Model SV-3 at a cross-head speed of 1mm/min using films of 2 cm long. Dynamic mechanical analysis (DMA) was conducted on ORIENTEC Automatic Dynamic Viscoelastomer Rheovibron model DDV-01FP at 35Hz at a heating rate of 4°C/min. Thermogravimetric analysis (TGA) was performed with Rigaku Thermo Plus 2TG-DTA TG8120 at a heating rate of 5°C/min under argon.

2.3 Preparation of PI-PDMS Hybrids by Sol-Gel Process

The PI-PDMS hybrids were prepared in 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 H_2O =1:2) was then added and stirred about 24 hrs. The solution was cast on glass plates, dried in air oven at 60°C/16 h, 100°C/1h, 200°C/1h, 300°C/1h, 350°C/15 min. to obtain solid films. Pristine PI, PI-PMPS and PI-PDPS hybrids were prepared in the similar way by using DEMPS and DEDPS as PSX, respectively.

The molecular weight of the inorganics was measured by SEC (Fig.1). The inorganics were collected by heating the small pieces of hybrids at 40°C/72h in THF. The M_w/M_n were 1702/1640(=1.03), 1673/1627(=1.02), 1580/1572(=1.00), for PDMS in PI-PDMS(5%), for PMPS in PI-PMPS(5%), for PDPS in PI-PDPS(5%) hybrids respectively, which indicated that oligomers were produced in PI-PSX hybrids.

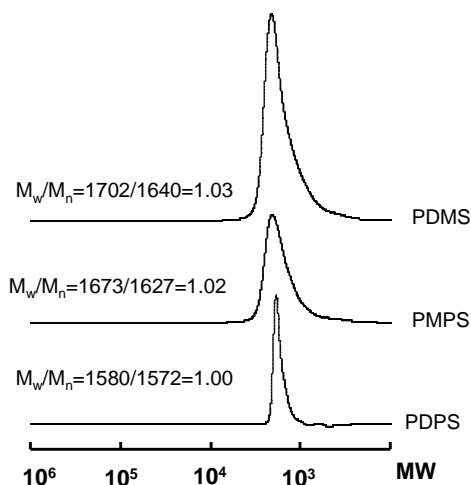


Fig 1. SEC curves of the oligomers in PI-PDMS(5%), PI-PMPS(5%), PI-PDPS(5%) hybrids

Imidization and curing of the hybrids were checked by IR. 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 imidization. The increased absorption peak related to Si-O-Si at $1000\text{--}1100\text{cm}^{-1}$ in comparison to pristine PI proved the sol-gel reaction and presence of PSX in hybrids.

Completion of imidization was confirmed by DSC also. In case of all hybrids, endotherm happened due to imidization of PI mainly. After final curing, endotherm disappeared and polymerization was completed. IR-spectras of the hybrids also shown the characteristics picks related to PI arise after 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 presence of 5, 10, 20, 50% PSX. After increasing the contents of inorganics, the amount of endotherm became lower. This results supported the increasing Si-O-Si related absorption in IR spectra. The amount of endotherm related to PI-PDPS hybrids are lower than those of PI-PMPS, PI-PDPS hybrids due to crystalline in nature of PDPS which also confirmed by XRD.

2.4 Morphology of PI-PSX Hybrids

XRD patterns of different PI hybrid films were measured. In case of PI-PDMS and PI-PMPS hybrids, XRD patterns are similar to the XRD pattern of pristine PI. But, PI-PDPS(20, 50%) hybrids showed clear peak

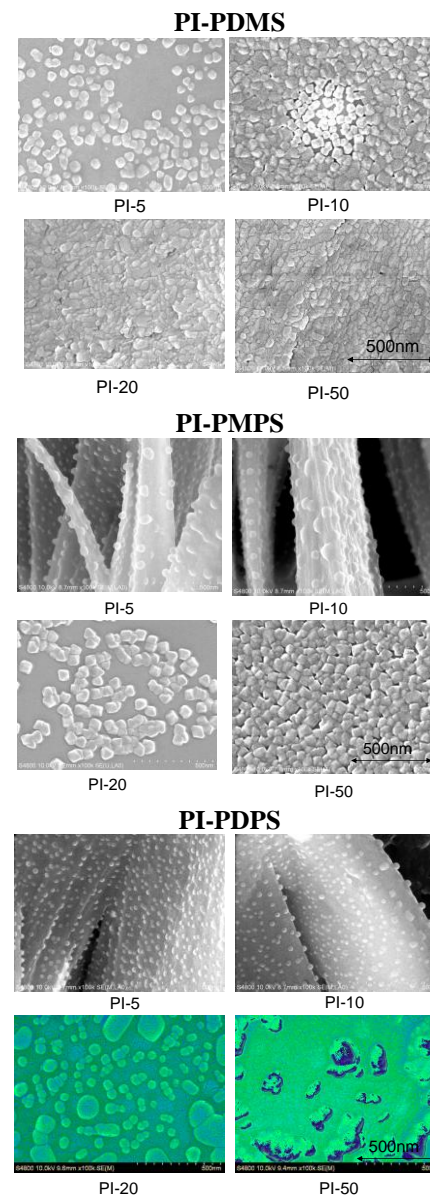


Fig 2. SEM-images of various PI-PSX hybrids

at around 5 to 15 ° due to the crystal structure of PDPS.

The shape and size of inorganics in various PI-hybrids were seen by SEM (Fig. 2). SEM-images were taken from etching system. In PI-PDMS hybrids, the inorganic particle size were about 15-100 nm in case of PI-5%PDMS hybrids. The particle became aggregated at high contents (10-50%). The inorganic particle sizes were about 15-100 nm and became aggregated at high content (20, 50%) in case of PI-PMPS hybrids. In PI-

5% and 10% PDPS hybrids, 15-65nm well distributed PDPS particles were seen. These particles became severe aggregated and aggregated particle size became up to 375nm. The XRD pattern also confirms the presence of big crystal in hybrids.

3. RESULTS AND DISCUSSION

3.1 Optical Properties of PI-PSX Hybrids

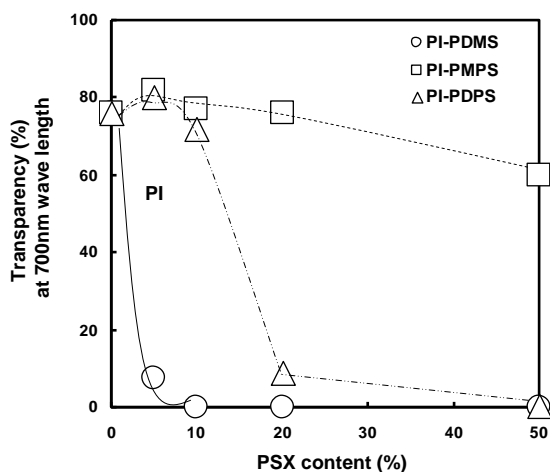


Fig 3. Effect of PSX on Transparency (%) of PI-PSX Hybrids

The transparency of the hybrids were checked by UV-spectrophotometer (Fig. 3). 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 pale yellow colour 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. π - π interaction between PI and phenyl side group related PSX 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 PSX reduced transparency due to the aggregation of inorganics which seen in SEM-images. In case of higher contents of (20, 50%) methyl related hybrids, the inorganic made a layer in film which hinder the light to pass and made the film opaque. But PI-hybrids with higher (50%) PDPS contents made bigger ball like inorganic particle in stead of layer which allow light to pass through the film and the hybrid film became transparent up to PI-PDPS(50%) hybrids.

3.2 Tensile Performance of PI-PSX Hybrids

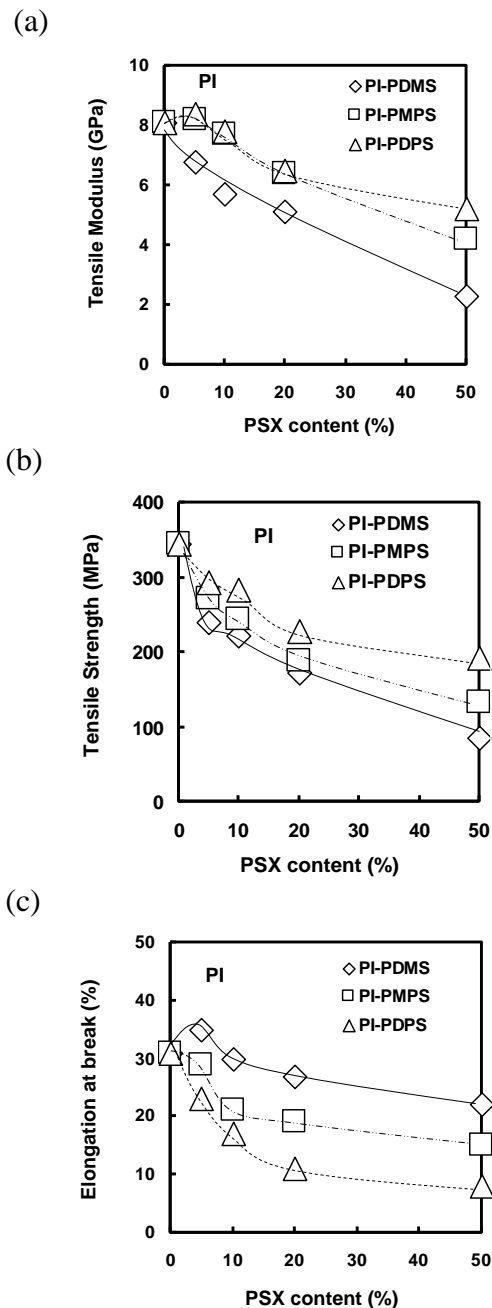


Fig 4. Effect of PSX on tensile performance of PI-PSX hybrids (a) Tensile modulus (b) Tensile Strength (c) Elongation at break (%)

The mechanical properties of PI and PI-PSX hybrids were tested by stress-strength tests (Figure 4). 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 tensile strength. In case of PI-PDPS and PI-PMPS hybrids, the modulus of PI-5 hybrids increased than pristine PI due to the rigidity of side aromatic functional group related hybrids and phenyl-phenyl 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 phenyl-phenyl interaction than PI-PDMS hybrids. The brittle behavior of phenolic group decreased the elongation at break% of the PI-PDPS and PI-PMPS hybrids.

3.3 Dynamic Mechanical Analysis (DMA) of PI-PSX Hybrids

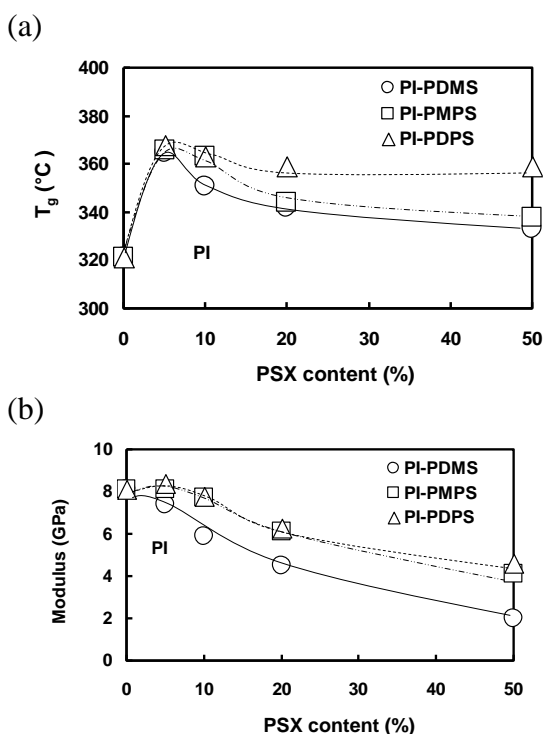


Fig 5. Effect of PSX on (a) Glass transition temperature (T_g) from $\tan\delta$ and (b) Tensile modulus at 30°C of PI-PSX hybrids

DMA was done mainly to observe the glass transition temperatures of the hybrid (Fig. 5). 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 (Fig.8a). 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.

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 phenyl-phenyl interaction and H-bonding between PI and PSX 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 phenyl-phenyl interaction between PI, PSX phases. Even PI-5%PDPS hybrids showed higher modulus than pristine PI at 30°C due to the crystalline structure of PDPS which was shown in XRD.

3.4 Thermal Gravimetric Analysis (TGA) of PI-Polysiloxane 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 [8-9]. From figure 6, it suggested that phenyl related PI-PSX hybrids provided higher char

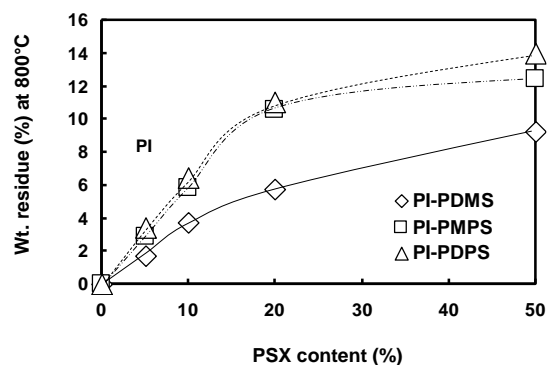


Fig 6. Weight residue (%) under air of various PI-PSX hybrids

yield (%) than that of methyl related PI-PSX hybrids after degraded at 800°C under air. All PI-PSX hybrids have higher thermal stability than pristine PI. In case of our PI-PSX hybrids, TGA under argon was done to check the thermal stability of PI-PSX hybrids (Fig. 6). 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. PI-PMPS and PI-PDPS hybrids have higher char yield than PI-PDMS because of phenyl rigid aromatics (Figure 7).

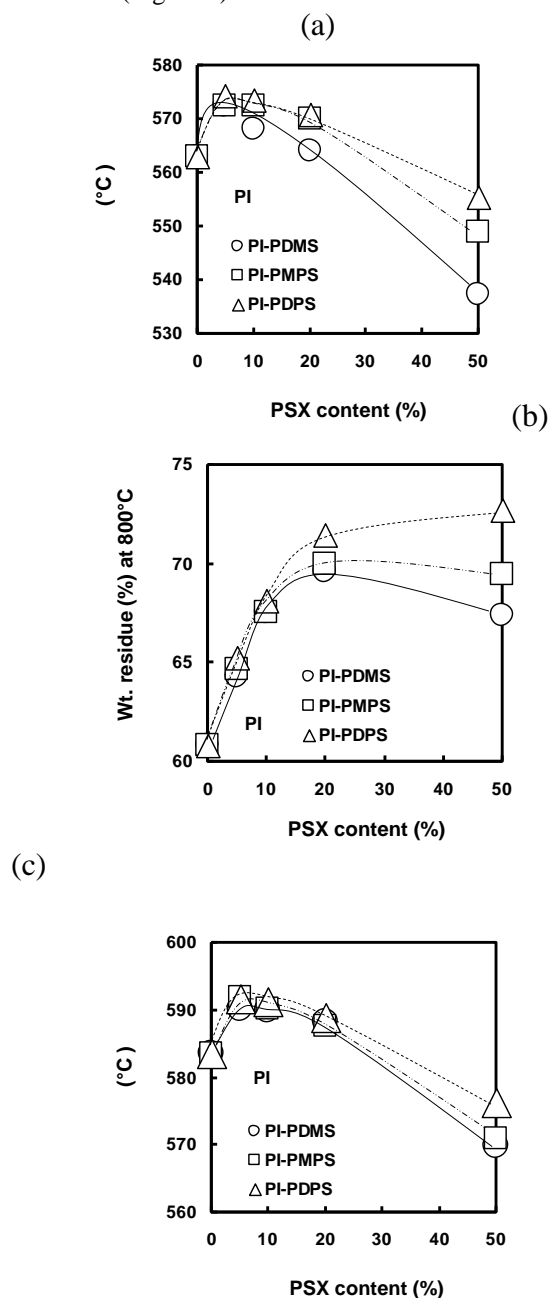


Fig 7. Effect of PSX on thermal properties of PI-PSX hybrids (a) T_5 (°C) (b) T_{10} (°C) (c) Weight residue (%) at 800°C

4. CONCLUSIONS

PI-PSX hybrids were prepared by PI and various ratio of PSX. Type of PSX showed pronounce influence on transparency, thermal and mechanical properties of the hybrids. In DSC, amount of endotherm of phenyl related PI-PSX hybrids were lower than PI-PDMS hybrids. PI-5(PDMS) provided higher elongation at break where as PI-5(PDPS) showed higher modulus than pristine PI. Small content (5%) of phenyl related PSX increased the transparency of the hybrid due to π - π interaction between organic-inorganic phases. The introduction of PDPS revealed the optimum enhancement of flame retardancy of PI. The inorganic enhanced the T_g as well. In-situ sol-gel process can provide PI-PSX hybrids successfully.

5. REFERENCES

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