

ORGANIC-INORGANIC TERNARY HYBRIDS: SYNTHESIS AND CHARACTERIZATION

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ABSTRACT

Ternary hybrids from polyimide, organically modified clay (OMMT) and diethoxydimethylsilane were prepared through insitu polymerization by sol-gel process. Poly(amide acid) were prepared from the reaction of pyromellitic dianhydride, 4,4'-oxydianiline. O-MMT was prepared by surface treatment of montmorillonite with ammonium salts of amines such as tyramine, phenylethylamine, aminolauric acid and dodecylamine. Differential Scanning Calorimetry showed that the inclusion of any type of OMMT lowered the onset and maximum temperature of PI. Amount of clay also have effect on onset and maxima of endotherm. Viscoelastic measurements expressed that the hybrid composites showed two T_g s. TGA showed that hybrid composites have delayed decomposition temperatures when compared with pristine PI indicating the enhancement in the thermal stability. Aromatic modifiers increase the 5% degradation temperature (T_5) and 10% degradation temperature (T_{10}) of the hybrids more than the aliphatic salts treated PI-hybrids. Presence of small OMMT (2%) in hybrid increase the modulus, strength and elongation than the pristine PI. Scanning Electronic Microscope images were observed to confirm the particle size of polydimethylsiloxane of the hybrids.

Keywords: Polyimide, Clay, Insitu sol-gel process

1. INTRODUCTION

Polymer hybrids have been receiving increasing attention because of the continued need for engineering polymers with improved properties. In hybrids, combination of organic-inorganic materials offer a mean of engineering into novel materials having certain combination of desired properties exhibited individually by each component materials. PI is well known as a high temperature engineering polymer. Comparing to most other organic or polymeric materials, PI exhibits an exceptional combination of thermal stability, mechanical toughness and chemical resistance. In addition, it has excellent dielectric properties because of its high degree of ductility and inherently low thermal expansion coefficient. Research interests in aromatic polyimides have increased in response to increasing high technology applications in many fields (eg: aerospace, automobile and microelectronics).

Polymer/inorganic nanocomposites based on the intercalation of polymer chains into organically modified layered silicates from a class nanocomposites that have recently received considerable attention, because they often exhibit superior physical, mechanical and thermal properties to conventional mineral – filled composites or unfilled polymers. Clay is a type of layered silicate, and the most commonly used clay in the preparation of polymer/clay nanocomposites is

Montmorillonite (MMT) in which galleries naturally exist inorganic cations, balancing the charge of oxide layers in a hydrophilic environment. The ion-exchange of these cations with the organic ammonium salts affords hydrophobic environment inside the galleries of MMT (OMMT)¹. The resulting organophilic galleries of OMMT will exchange the compatibility with polymers, improve the dispersion of the silicate layers into the matrix² and assist the penetration of monomers and/or polymers into the galleries.³ Also, organic ammonium salts can provide functional groups that can react or interact with the monomers or polymers to improve the interfacial strength between the reinforcement and the polymer matrix.⁴ The study on PI-clay nanocomposites were reported by many researchers⁵⁻¹⁰ and found that the dispersing of nanolayered clay, in the form of intercalation or exfoliation into various polymer matrices to increase the thermal stability, gas barrier, flame resistance and corrosion protection but decrease the elongation and increase brittleness.⁷ In these circumstances, the range of polymer properties and hence applications can be broadened by combining with another polymer (e.g. by blending or copolymerization). For example poly (imide-siloxane) copolymer show many properties such as low water absorption, chemical resistance, impact resistance.¹¹

In the current studies, we developed new kind of PI-clay-siloxane ternary hybrids based on various types of OMMTs. We also investigated the effect of the type and content of OMMT on the properties of our ternary hybrids. The introduction of polydimethylsiloxane (PDMS) into the PI-clay hybrid will be achieved via the sol-gel¹²⁻¹⁵ reaction of diethoxydimethylsilane into poly(amic acid), followed by thermal imidization. Both mechanical and thermal properties of the hybrids will be investigated then in details.

2. EXPERIMENTAL

2.1. Reagents

Kunipia-F, a Na-montmorillonite (MMT), was supplied by Kunimine Ind. Co., with cation exchange capacity (CEC) of 119 meq/100g. Dodecylamine, Aminolauric acid and 2-phenylethylamine hydrochloride and Tyramine were used as received. Pyromellitic dianhydride (PMDA) and 4, 4'-oxydianiline (ODA) were purified by sublimation. N-Methyl-2-Pyrrolidone (NMP) was dried by distillation under reduced pressure over calcium hydride. DEDMS was used as received. Poly(amide acid) (PAA) were prepared from the reaction of PMDA, ODA in NMP.

2.2. Preparation of OMMT

OMMT were prepared from MMT by ion exchange reaction using different ammonium chloride salts of tyramine (T), phenylethylamine (P), aminolauric acid (A) and dodecylamine (D) in water according to the reported method (Fig.1).⁷

2.3. Preparation of PI-Clay-PDMS hybrids under Sol-Gel process

The synthetic procedures for polymer-clay-PDMS hybrids with different types and ratio of OMMTs were very similar, only a representative example for the preparation of PI/T-MMT(2%)-PDMS(5%) is given: Into a 200 ml flask equipped with nitrogen inlet and mechanical stirrer, certain amount of PAA and OMMT (2% wt of the solid in PAA) were placed. The reaction mixture was stirred for 5 h at room temperature to give a transparent yellow viscose solution. The solution was stire some time after adding DEDMS (which is 5 % wt of equal mmol of PAA). Stirring was continue upto 24 hrs by adding distilled water (double mmol of DEDMS). The weight of TMMT was changed accordingly (1, 2, 3, 5%) to get different type of polyimide-TMMT hybrid solution. All the blends were cast on glass plates by using 700 μ m doctor blade, dried in vaccume oven at 60°C/12 hrs, 100°C/1 h, 150°C/1 h, 200°C/1h, 250°C/1 h, 300°C/1h, 350°C/1h to obtain solid films. Another 3 types of hybrids were made in where PDMS was 5% and 2% of AMMT, DMMT and PMMT.

2.4. Measurements

XRD was measured in reflection mode using a X-ray diffractometer, Rigaku, RINT2000 using CuK α radiation. The Scanning rate was 0.3°/min from 2 θ = 2 to 10. DSC

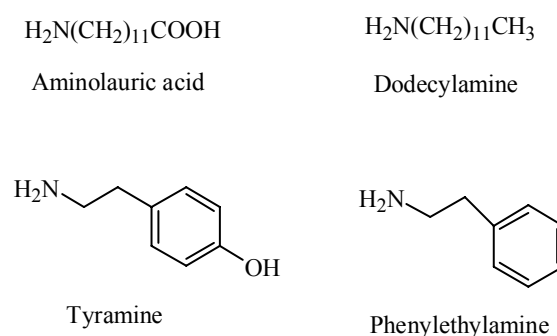


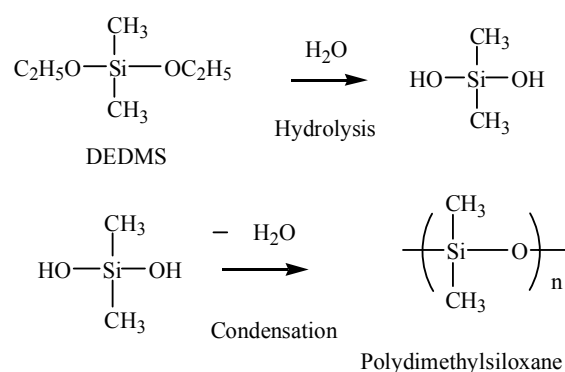
Fig 1: Intercalation agents of OMMT

was recorded using Rigaku Thermo Plus 2DSC8230 at a heating rate of 10°C/min under nitrogen. SEM of HITACHI S-4800 was used to see the domain size of PDMS. Dynamic Thermogravimetric Analysis (TGA) was performed with Rigaku Thermo Plus 2TG-DTA TG8120 at a heating rate of 5°C/min under argon. Dynamic viscoelastic measurements 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 at a crosshead speed of 1mm/min using films of 2 cm long. The tensile properties of each sample were determined from stress-strain tests.

3. RESULTS & DISCUSSION

3.1. Preparation of PI-clay-PDMS hybrid films

Sol-gel process is a common and convenient technique to develop homogeneous and high purity inorganic oxide at ambient temperature. In this process, silanol group was formed from DEDMS in the presence of water in hydrolysis process, and this silanol reacts each other to form PDMS in condensation step (Scheme 1). In this study, we employed this in-situ formed PDMS as a toughner for PI-clay nanocomposites. Carboxyl group of PAA act as catalyst inherently.



Scheme 1: Preparation of PDMS

3.1.1. Preparation of OMMT

The modification of the hydrophilic Na-MMT surface layers to become hydrophobic is the initial stage to disperse MMT uniformly into PI matrix. As a result of this surface modification, the surface of MMT will have a hydrophobic character. Thus, there will be hydrophobic

environment into the clay galleries to accommodate the hydrophobic poly (amic acid) due to the compatibility between them. In our study, we used two longer aliphatic modifiers (D and A) and two shorter aromatic modifier (P and T) for ion exchanging to prepare organophilic MMT (OMMT). The interlayer

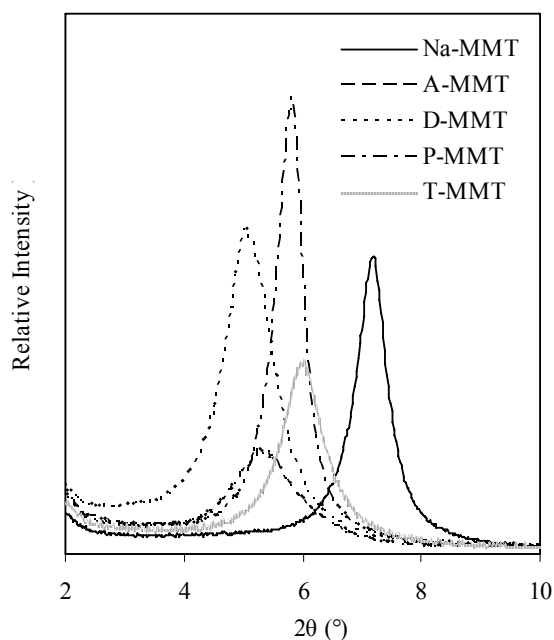


Fig 2: XRD of Na-MMT and OMMTs

spacing were calculated from X-ray diffraction (XRD) measurements shown in Fig.2 and summarized in Table.1. It is clearly shown that the interlayer spacing increase with the increase of the size of surfactant: from 0.28 for Na-MMT to 0.78, 0.69, 0.56 and 0.56 for A-MMT, D-MMT, P-MMT and T-MMT respectively.

Table 1: X-RD of OMMTs

MMT Type	Diffraction peak 2θ (°)	Basal spacing d (nm)	Interlayer Spacing (nm)
Na-MMT	7.22	1.22	0.28
A-MMT	5.38	1.64	0.78
D-MMT	5.04	1.75	0.69
P-MMT	5.78	1.51	0.56
T-MMT	5.84	1.51	0.56

3.1.2. Thermal Stability of OMMT

The thermal stabilities of Na-MMT and OMMTs were investigated by TGA. The T_5 and T_{10} temperatures of the A-MMT, D-MMT, P-MMT and T-MMT were 287, 305, 493, 506 °C and 328, 350, 689, 667 °C respectively. From the curves, we found more than one step degradation in the temperature range of 200-600°C in case of OMMTs. Same phenomenon was observed by Zhu-Mei et al⁸ and can be stated that the organics which transferred from salt to Na-MMT were used for organic-inorganic intercalation during synthesis of PI/Clay/PDMS hybrids. From the table, we also can stated that the aromatic modifier provide less organics (13.2, 14.3 %) than the

aliphatic modifier (22.9/19.6 %) which may influence the thermal stability of the PI hybrids.

3.2. Curing behaviour of the Hybrids

Curing behaviour of the films were studied by DSC also in graph. The endothermic reaction happened due to the imidization. At 300°C, the DSC curve shows straight line which shows completion of polymerization. Explanation of DSC scans of poly(amide acid) cast films is complicated because the endotherm include imidization reaction, heat of decomplexation of poly(amide acid)/solvent and residual solvent evaporation from poly(amide acid) films.⁷

The onset, maxima of endotherm and amount of endotherm of the pristine PI were 122, 157 °C and 50.84 cal/g which became 106, 144 °C and 37.50 cal/g for A-MMT; 106, 142 °C and 30.10 cal/g for D-MMT; 113, 153 °C and 46.25 cal/g for P-MMT and 113, 153 °C and 40.25 cal/g for T-MMT (Fig.3) after 100°C/1h curing. It can be stated that all type of OMMT decrease the onset, max. of endotherm and amount of endotherm than the pristine PI. There is a tendency that amount of endotherm related to longer modifier is lower than the shorter modifier. The longer aliphatic modifier expanded the clay galleries more than the shorter aromatic modifier which assisted the dispersion of OMMT into the matrix and allowed the monomer to penetrate easily into the galleries. After adding T-MMT in hybrids, the onset,

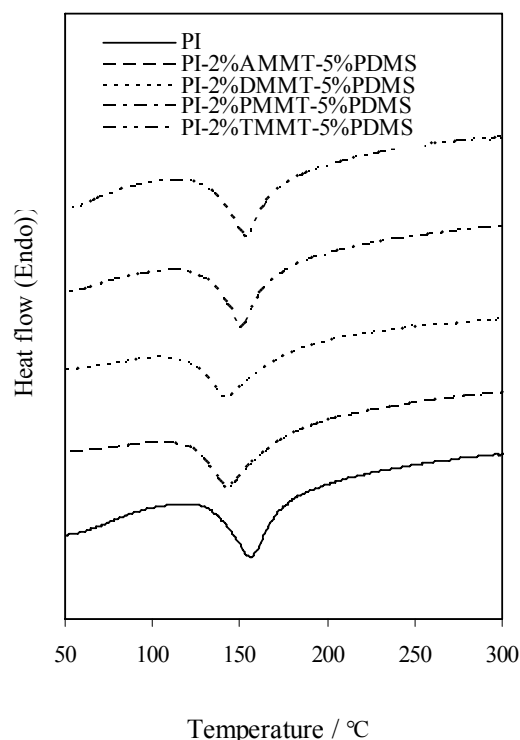


Fig 3: DSC of PI-hybrids after curing 100°C/1h

maxima of endotherm and amount of endotherm changed to 114.66, 156.49 °C and 46.67 cal/g for 1%; 112.53, 153.23 °C and 40.25 cal/g for 2%; 110.43, 151.77 °C and 35.91 cal/g for 3%; 109.83, 149.93 °C and 31.91 for 5% T-MMT (Fig.4) after curing 100°C/1h. Interestingly, we found that the incorporation of OMMT upto 5% into poly(amide acid) shifted the amount of endotherm to

lower range which considered because of the catalyzing effect of clay for imidization process.

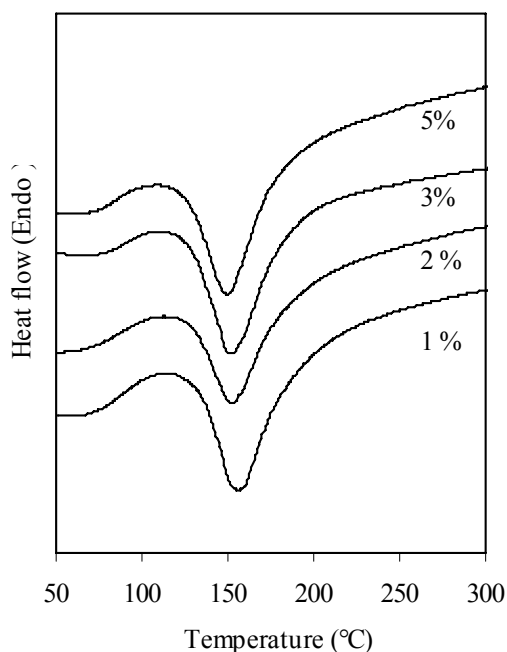


Fig 4: DSC of PI-TMMT hybrids after 100°C/1h curing

3.3. Morphological study

The films were quite transparent for PI-OMMT nanocomposite films with clay loading upto 3%. At high clay content (above 5%), transparency was reduced because of aggregation^{16,17}. XRD patterns of different PI hybrid films are shown in Fig.5. The peak related to OMMT disappeared in the hybrid upto 3% clay suggesting the disorder and loss of structure regularity of the clay layers. Thus we may can consider that the 0.96 nm-thick clay layers are exfoliated and disappeared at the molecular level into PI hybrid. But incase of PI-5% clay and 5% PDMS, XRD pattern showed small pick which were related to aggregation of OMMT.

The size of PDMS particles in the hybrids were observed by SEM. In all PI-2-5 hybrids, the particles were circular in shape and size about 30-40nm which transparent the hybrid films. The round shape of the particles lower inter-particle gap and provide better compactness. The domain size of PDMS became about same after adding different ratios of OMMT (1-5%).

The thermal stabilities of PI and their hybrid composites in argon were studied by TGA. Inclusion of 1, 2, 3 and 5% OMMT increased the T_5 temperatures from 537°C to 538, 555, 554, 545°C and T_{10} temperatures from 558°C to 561, 569, 568, 564 °C (Fig.6). The wt. residue (%) of pristine PI at 800°C was 54.8% which became 55.8, 57.9, 58.4, 60.3 % after adding different ratio of OMMT accordingly. The addition of small amount of OMMT increase the T_5 , T_{10} temperatures than the pristine PI which may result from the barrier effect of the OMMT layer structure, as well as the strong interaction between the organoclay and PI molecules.¹⁵ Two steps degradation were occurred – first stage appeared during 350 to 400°C for PDMS, and the second stage appeared above 500°C because the degradation of imide backbone.¹⁸ Presence of different OMMT at 2% acted

differently on thermal behaviourly of PI. Aromatic modifier increase the T_5 and T_{10} temperatures more than the aliphatic modifier. Inclusion of 2% T-MMT and P-MMT increased the T_5 and T_{10} temperatures 545, 564 °C and 555, 569 °C. After adding the same ratio of aliphatic modifier T_5 and T_{10} temperatures were 538 and 560 °C incase of A-MMT and 538 and 561°C incase of DMMT (Fig.7). Above 3% OMMT resulted to lower thermal stability than other hybrids because of aggregation.¹⁹

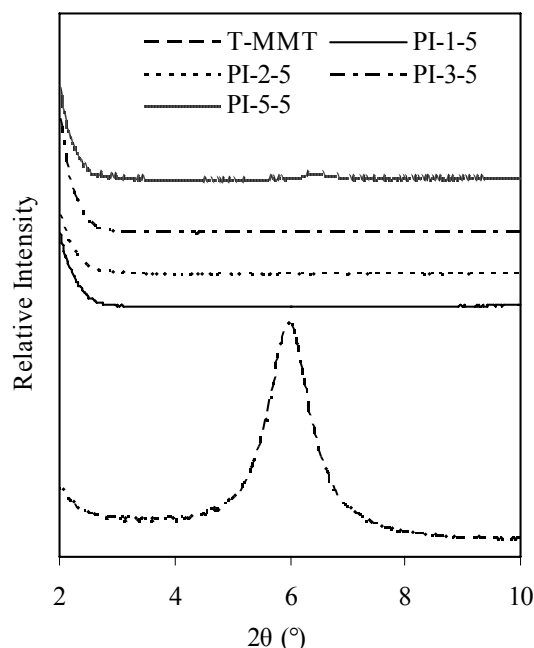


Fig 5: XRD of OMMT, PI-TMMT and PI-OMMT-PDMS hybrids

4. PROPERTIES OF PI-CLAY-PDMS HYBRIDS

4.1. Thermal properties

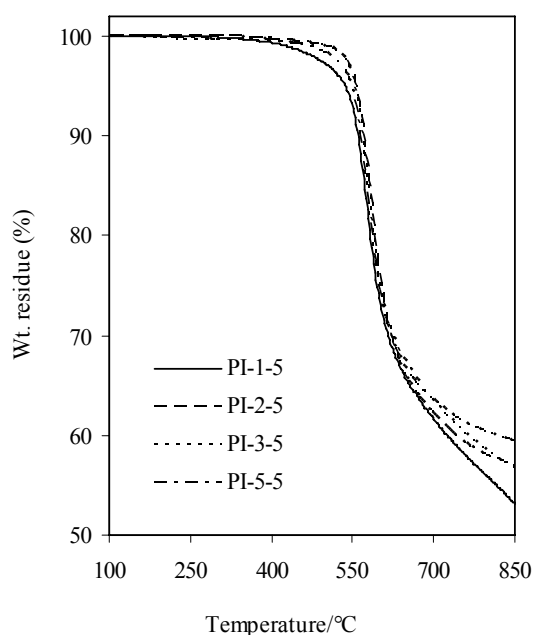


Fig 6: TGA of PI-TMMT hybrids

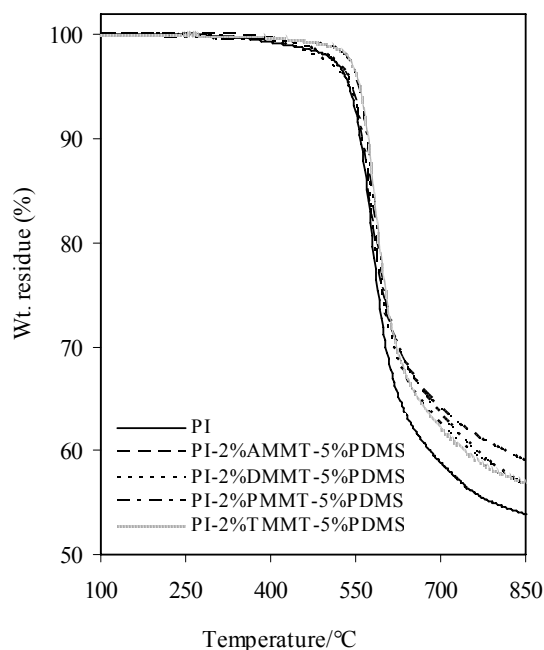


Fig 7: TGA of PI, PI-OMMT-PDMS hybrids

4.2. Tensile properties

The results of tensile test for different PI films are summarized in Table 2. The tensile modulus and tensile strength of the pristine PI was 2.2 GPa and 58.2 MPa. In the case of PI-TMMT-PDMS hybrids, more ratio of OMMT increase the tensile modulus and strength at every stage. Inclusion of only 2% T-MMT and 5% PDMS increased toughness of the PI hybrid film by achieving 4.95 GPa tensile modulus, 86.39 MPa tensile strength and 48.33% elongation at break. This result clearly demonstrate that the PDMS worked effectively as toughener for the PI-clay. Each type of OMMT at 2% wt. ratio reflects same characteristics in presence of 5% PDMS which were the feedback of PI-2%clay composites. More addition of clay (5%) reduced the tensile modulus, strength and elongation which were related to phase separation.

4.3. Viscoelastic properties

Viscoelastic analysis of the PI-hybrids are shown in Fig.8. The glass transition temperatures (T_g) of the films estimated from the maximum of E'' and $\tan\delta$. Two T_g s were found in all hybrids related to each OMMTs – the lower T_g is based on the PDMS component and the higher T_g based on the PI component. In PI (PMDA/ODA)-clay composite, T_g s are more than 400°C. The lower T_g of PDMS decreased the T_g of the hybrids. In case of $\tan\delta$, the higher T_g s became 392, 394, >400, 392°C and lower T_g s became -74, -72, -69, -76°C after implement of 1, 2, 3 and 5% T-MMT (Fig.8). Inclusion of 1, 2, 3 and 5% T-MMT and 5% PDMS made the higher T_g s 378, 380, 386, 383 °C and lower T_g s -80, -80, -78, -73 °C incase of loss modulus.

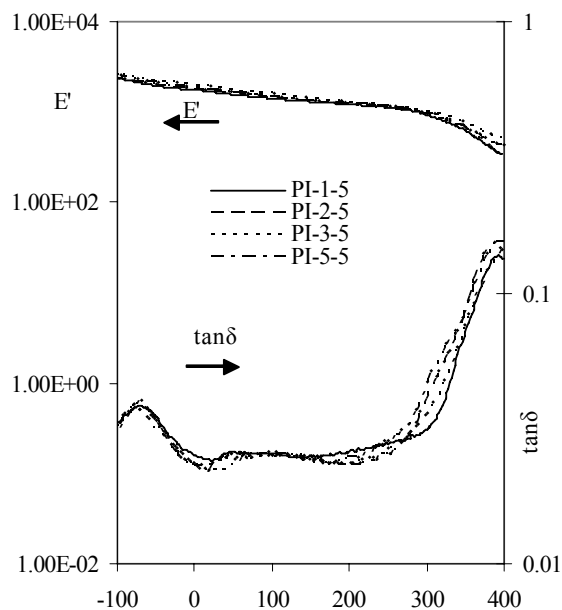


Fig 8: DMA of PI-TMMT hybrids

Table 2: Tensile properties of PI-hybrids

Type of PI	Tensile modulus	Tensile strength	Elongation
PI-OMMT-PDMS	(GPa)	(MPa)	(%)
Pristine PI	2.2	58.2	36.4
PI-1%T-MMT-5	4.6	80.1	32.3
PI-2%T-MMT-5	4.9	86.4	48.3
PI-3%T-MMT-5	4.9	88.4	28.8
PI-5%T-MMT-5	3.5	78.6	18.5
PI-2%A-MMT-5	5.1	88.5	47.1
PI-2%D-MMT-5	4.6	83.9	47.4
PI-2%P-MMT-5	4.7	80.4	46.3

5. CONCLUSIONS

Polyimide/clay/PDMS ternary hybrids were made successfully by using various types and ratios of OMMT through sol-gel process. The curing behaviour of PI depend on the type of functional group of modifier. Hybrids were more thermally stable after modified through aromatic modifier than aliphatic modifier. Ratios of OMMT effect the thermal behaviour as well. Amount of OMMT effect on the T_g s of PI and PDMS. Different ratio of OMMT increase the tensile modulus and strength effectively. At 2% clay loading, PI-clay-PDMS hybrids showed best balance in properties concerning thermal stability, strength, modulus, elongation due to the homogeneous dispersion of clay and toughening effect of PDMS.

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