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Effect of Silica and Titania ternary hybrid on the mechanical, thermal and optical behavior of the Polyimide

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A B S T R A C T

Polyimide/silica/titania hybrid films were prepared via sol-gel process. Poly(amic acid) solutions were prepared by mixing pyromellitic dianhydride (PMDA),4,4'oxy dianiline(ODA)and N,N-dimethyl acetamide(DMAc) solvent through *in situ* polymerization method. Silicic acid and titanium tetrachloride are the respective precursors used for the silica and titania. The absorption band of Si-O-Ti bonds in FTIR spectra of the hybrid films revealed the formation of hybrid inorganic network between silica and titania. The glass transition temperatures of the hybrid samples were higher than pure polyimide. Scanning Electron Microscopy (SEM) results indicated the formation and dispersion of nanometer scale size of inorganic domains inside the polyimide matrix due to the introduction of silica stabilized TiO_2 and the interactions between organic and inorganic phases .The studies on the optical properties of the hybrid films indicate red shift of the absorption band that increased with increased TiO_2 content. The pretty thermal stability and tunable optical properties may provide the potential applications of the polyimide-silica-titania hybrid films in optical devices.

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1. Introduction

In recent years, many efforts have been made on the organic-inorganic nanocomposites that can be used to improve the mechanical and thermal properties of polymers by the addition of inorganic additives. The challenges in this area of high performance organic–inorganic hybrid materials are to obtain significant improvements in the interfacial adhesion between the polymer matrix and the reinforcing material since the organic matrix is relatively incompatible with the inorganic phase.

In general, the smaller the size of the inorganic particle, the larger it's available surface area for enhancing the reinforcement of the continuous organic phase while simultaneously improving macroscopic homogeneity and optical properties. Recent advancements in nanotechnology have opened a new era in the synthesis of organic-inorganic hybrid nanocomposites, with nanosized inorganic particles. Furthermore, the hybrid nanocomposites show its capability towards special application where characterization and properties play a vital role [1-3].

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Polyimides are often based on stiff aromatic backbones and characterized by their superior thermal stability and mechanical strength[4-6]. They have been widely used in microelectronic and aerospace applications[7-10]. The mechanical and thermal properties of polyimide polymers can be further enhanced or tailored to meet widely varied demands by combining them with various inorganic metal oxides[11] by *in situ* polymerization and sol-gel process[12,13]. These processes have been adapted to the preparation of organic-inorganic hybrid nanocomposites. It has been shown that the morphology of the resulting metal oxides in the composites may be improved by tuning the formulation and processing conditions.

Recently, several studies have been carried out by different researchers for the preparation and characterization of binary hybrid nanocomposites, such as PI/SiO_2 and Pi-TiO_2[14-20]. This has been reported that preparation of binary hybrid films of poly (imide siloxane) PIS/SiO_2 and PIS/TiO_2[21]**.** Further synthesizing of PIS/Silica hybrid nanocomposites a 'C-Si' covalent bonding enhancing the dissociation of the inorganic SiO_2 in the organic phase where as the particle size is found to be <60nm.This type of introduction significantly improved the mechanical and thermal properties**.** A similar method has also been applied for the preparation of PIS/titania (TiO_2) hybrid nanocomposites[22]**.** TiO_2 is well dispersed in a PIS matrix by the sol-gel process to keep the particle size below 50nm(TiO_2 content<20wt%).The nanocomposite exhibited good optical transparency where as the mechanical and thermal properties were only significantly compromised.

Another category of PI-metal oxide hybrid nanocomposites is the ternary hybrids of PI/SiO_2-TiO_2.In this category SiO_2 contributes towards good thermal stability whereas TiO_2 contributes smaller particle size and an adjustable refractive index[23]**.** Wang etal.[24] prepared PI/SiO_2-TiO_2 hybrid films through a non-hydrolytic sol-gel route from the silicic acid and titanium tetrachloride. The optical properties of the hybrid films exhibited a red shift of the absorption band that increased with increasing TiO_2 content maintaining good optical transparency. The thermal decomposition temperature of the ternary hybrid films decreased slightly with increasing TiO_2 content. However, Qiu et al.[25] prepared ternary hybrid PI/SiO_2-TiO_2 films with SiO_2 to TiO_2 ratios of 1:2, 1:1&2:1 and found that such ternary hybrids exhibited desirable optical properties without significantly sacrificing physical and thermal properties. In general, the well known role of SiO_2 in polyimide nanocomposite materials is to enhance the thermal and mechanical properties. On the other hand, incorporating TiO_2 is known for its better functionality and optical property modulation with controlled particle size. However, because of its photo catalytic character, the presence of TiO_2 tends to decrease the thermal stability of the material[26].

It is quite likely that combining the two would complement each other, thus widening the range of design variables, as has been shown by various literature survey[25-27]

In this report, we proposed a new systematic approach through non hydrolytic sol-gel method to understand the ternary PI/SiO_2/TiO_2 hybrid nanocomposite keeping view towards the industrial aspect, a step forward has taken to study the effect of SiO_2-TiO_2 ratio on the thermal degradation temperature. At the same time study of Si-O-Ti bond will help to explain the role of 'Si' and 'Ti' in the nanocomposites. Dispersion of inorganic particles and optical properties of the composite will be discussed. The structural, thermal, and optical properties of the resulting hybrid have been studied. The results show that PI/SiO_2/TiO_2 nanocomposites have potential application in the optoelectronic devices [28-38].

2. Materials and methods.

2.1 Materials

4,4'-oxydianiline (ODA, chemical reagent grade), and pyromellitic dianhydride (PMDA, chemical reagent grade)were purchased from Abbron chemicals, Hyderabad and used as received. N,N-Dimethyl acetamide (DMAc, chemical reagent grade),Sulfuric acid(analyticalreagentgrade),Tetrahydrofuran(THF), Titanium tetrachloride($TiCl_4$), ammonium hydroxide (35%)(NH_4OH), ethylene glycol, water glass(highly purified, containing Na_2O and SiO_2) were all purchased from Sigma Aldrich, India and were used as received.

2.2 Preparation of silicic acid precursor

The silicic acid was prepared by taking the modified form of Abe's method[39] in which a 3.2M water glass solution was treated with 1M H_2SO_4 maintaining the pH= 2 under stirring at ambient conditions. Then equal volume of tetrahydrofuran was added to the mixture after saturating with sodium chloride and stirred for 2 hour. Then the mixture was stored at 10^0C for half an hour. After that the organic layer was separated and dried. The silica content of the silicic acid oligomer-THF solution was determined to be 15.51wt% by TGA, assuming that all the silicic acid was transformed into silica at 800^0C[40], the end point of the test.

2.3 Preparation of titania precursor

With vigorous stirring, titanium chloride (2ml) was mixed drop wise in ammonium hydroxide/ethylene glycol in a 100ml beaker. The stirring was continued for another 10mins. The reaction was exothermic and carried out in 100 ml beaker. Then, this mixed precursor was heated to 333K.

2.4 *Preparation of silica/titania precursor*

The Silicic acid—Tetrahydrofuran solution and the $TiCl_4$-Ethylene glycol solution were mixed and stirred at room temperature for 3 h and then refluxed at 100⁰C for another 4 h.

2.5 Preparation of polyimide/silica/titania hybrid films

A required amount of silica/titania precursors were introduced to the poly (amic acid) solution and were mechanically stirred at room temperature for 6 h to obtain a uniform and transparent solution. Then the solution was cast on a glass substrate and dried at 60⁰C for 3 h, 100⁰C for 1 h, 200⁰C for 1 h and 300⁰C for 4 h, respectively.

3. Characterization

Tensile strength and modulus of the thin films by using an Universal testing machine(UTM), 3382, Instron UK, according to ASTM D638 method. FTIR spectra of the hybrid films were recorded on a Nicolet 6700 FTIR spectrophotometer. UV-Vis spectra were measured on a Perkin-Elmer Lambda 750 UV/Vis spectrometer using the wavelength from 200 to 900nm.The morphologies of the liquid nitrogen fractured surfaces of the PI/SiO_2/TiO_2 hybrid films were observed with a EVO MA 15, Carl Zeiss SMT Scanning electron microscope. Thermal gravimetric analyses(TGA) were performed on a Q 50,TA instruments, thermal gravimetric analyzer at a heating rate of 10⁰C/min in air and the temperature range was from 25 to 800⁰C. Differential Scanning Calorimetry were performed on a Q20,TA Instruments, DSC at a heating rate of 10⁰C/min in air and the temperature range was from 50-450⁰C.

4. Results and Discussion

4.1 Mechanical properties

The mechanical properties of PI and PI/TiO_2/SiO_2 hybrid composite films were studied and represented in Table-1.The tensile strength, elongation at break, tensile modulus of the hybrid films with respect to PI are discussed. This property is found to be more prominent in case of PI hybrid composites with 5wt% of inorganic content with a molar ratio of 9:1(TiO_2/SiO_2) as compared to other hybrid samples. However, a decrease in modulus to about 27% was observed with respect to virgin polyimide as represented in Table-1.

Table 1. Tensile test for polyimide and its hybrid composites

Sample code	Tensile strength	Tensile modulus (MPa)	Elongation at break (MPa)	Tensile strain at break (Mpa)
PI	92.38	3637.49	85.85	5.6
PITS-1	77.87	2648.63	46.94	18.71
PITS-2	26.94	1141.38	26.94	3.28
PITS-3	35.57	1349.48	35.48	5.13
PITS-4	22.11	856.11	22.01	4.16

It can be also seen that the strength of hybrid composites decreases with increase in inorganic domain with decreased molar ratio of titania and silica. This decrease in mechanical properties may be due to the strong interaction induced by inorganic domain (titania and silica) affecting the crystallization of PI. Similar results also indicated by Wang et al.[41]. In this experimental study of polyimide/silica nanohybrids from silicic acid oligomers. It was suggested by the several researchers that the adverse effect could be improved partly by the introduction of covalent bonding between the organic and inorganic phases using a suitable compatibilizer. However, it was seen that the presence of excess amount of compatibilizer may affect the crystallization of polyimide [42].

4.2 Thermal properties

The TGA and DTG curves of PI and PI/SiO_2/TiO_2 hybrid nanocomposite films are shown in the Fig.-1 and Fig.-2, respectively. The temperature at 50wt% loss and the residual ashes at 700⁰C are shown in the Table-2.The thermo gravimetric curve of the silica shows the total transformation of silicic acid to silica at 800⁰C. It was shown in the table that the final degradation temperature of the hybrid film was more in comparison to virgin polyimide. The char yield of virgin polyimide is found to be 6.26% which may be due to the stiff aromatic backbones present in the polyimide.

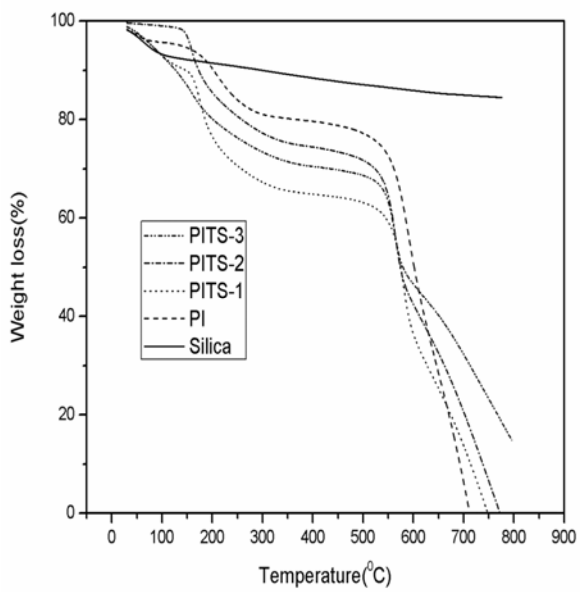

Fig. 1 TGA curve of PI, PITS-1, PITS-2,PITS-3 and Silica.

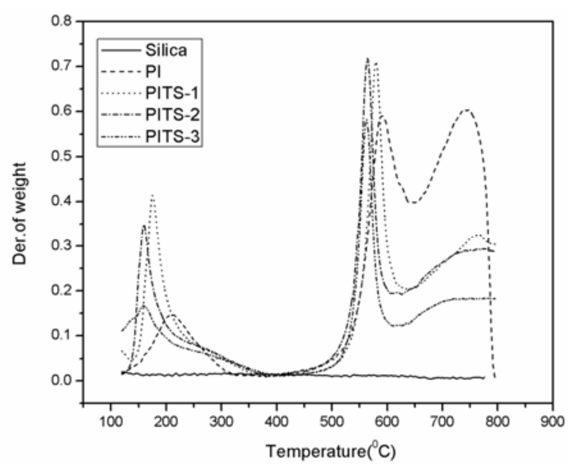

Fig. 2. DTG curve of PI,PITS-1 ,PITS-2 ,PITS-3 and Silica.

The char yield of the hybrid sample is increasing regularly and found to be maximum for the 7wt% hybrid sample. There is a regular increase in the final degradation temperature by decreasing the molar ratio as shown in the Table-2 but there is a decrease in degradation temperature at 50 wt% loss of the sample [B] in comparison to sample [A]and then regularly increases for the sample [C] to [D].

The introduction of TiO_2 causes only a little decrease in thermal degradation temperatures of the hybrid films compared to pure polyimide according to the results of Liu's [43].

Table 2. Degradation temperature & ash content of PI&PI/TiO_2/SiO_2 hybrid films.

Sample	Molar ratio	Initial degradation temp	Degradation at 50 %wt. loss	Final degradation temperature
PI	-	209.2	601.47	744.45
PITS-1	9	169.53	569.30	758.87
PITS-2	6.5	159.43	573.41	762
PITS-3	4.5	157.99	579.04	765

The reason for decreased thermal stability of hybrid films containing TiO_2 may be due to the metal catalyzed oxidative decomposition[44-45].The reason for the decrease in degradation temperature is due to the incomplete imidization process[46] that happened because of the chelating ligand in case of PI/TiO_2 hybrid nanocomposites. Another reason may be due to the catalytic role of TiO_2 that is happened in this case.

Thermal degradation of pure PI proceeds in 3 steps. The 1st step is initiated by the degradation of the imide monomers inside the polymer matrix and starts at 200-220^{0}C, depending on the heating rate. The 2nd step (600-620^{0}C) is initiated by the scission at the imide chain end units and the 3rd step above 600^{0}C by random scission within the polymer chain. PI weight loss above 200^{0}C indicates head to head linkages between N-H and C=O functional groups. The char residue of the hybrid nanocomposites increases with the increase in inorganic content inside the polymer matrix as represented in Table-2. The increase in final weight residues suggests the successful incorporation of higher amount of silica and titania into polymer backbone.

4.3 Thermal properties(DSC)

The Fig. 3 represents the DSC curves of PI and PI/TiO_2/SiO_2 films.The introduction of the TiO_2-SiO_2 composite particles increases the glass transition temperature from 158.43^{0}C for the PI to 175.91^{0}C for the PI/TiO_2/SiO_2 hybrids containing 5wt% inorganic domain.The reason behind the increase in T_g may be

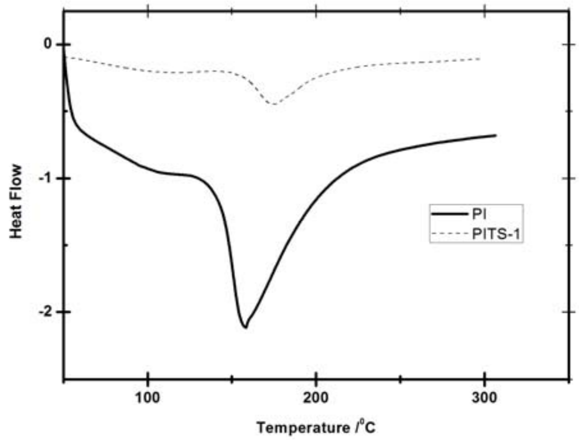

Fig. 3 Scematic diagram for DSC curves of PI and PITS-1 hybrid film.

due to the the strong interaction between PI and the gel particles that act like a physical cross linking points. In the sol-gel process,[47-48], the hybrid material may have attained the interpenetrated network that control the segmental movement of the PI and hence increases the T_g. The researchers have found that there would be a decrease in the thermal stability due to the introduction of TiO_2 as in the previous studies[49]. Simultaneously, due to the introduction of SiO_2, there would be an increase in the thermal stability as well[50].

4.4 FTIR measurements

The FTIR spectra of the PI and PI/SiO_2/TiO_2 hybrid nanocomposite films are shown in the Fig. 4.

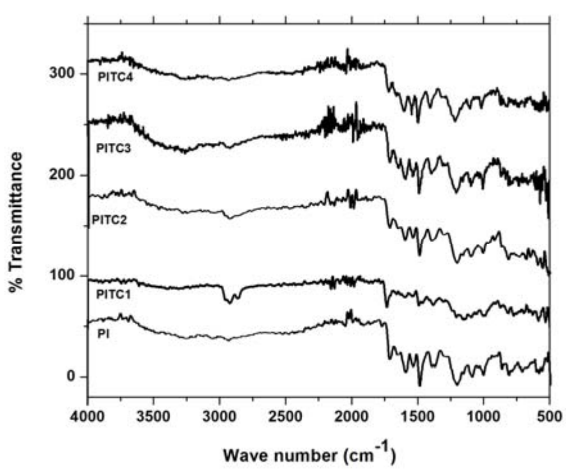

Fig. 4 FTIR study of PI, PITS-1, PITS-2, PITS-3, PITS-

PITS-5

The characteristic peaks at 1723cm^{-1} and 1392cm^{-1} show the symmetric C=O stretching and asymmetric C-N stretching of the imide group. After the introduction of inorganic contents, it can be observed that the broad and strong absorption bands in the range of 500-873cm^{-1} that corresponds to Ti-O-Ti network, and 924-1109cm^{-1} corresponding to Si-O-Ti and Si-O-Si network can be enhanced with increasing TiO_2 and SiO_2 content [51-52]. This proves the formation of the chemical bonds between SiO_2 and TiO_2 moieties. The characteristic peak at 2962cm^{-1} shows the residual Ti-OH and Si-OH groups in the hybrid films[53].There is no absorption near 1650cm^{-1} for the carbonyl group of Poly(amic acid) and indicates the complete imidization. Hence, it is proved that there is no interference of inorganic composites with the imidization process of poly (amic acid).

4.5 SEM analysis

The prepared PI/silica/titania ternary hybrid nanocomposite containing 5wt% inorganic content(9:1 molar ratio) indicates a homogeneous dispersion inside the polyimide matrix as it is shown in the Fig.-PIST-1. Other researchers found the inhomogeneous dispersion due to the poor compatibility between the organic and inorganic phases in case of PI/Silica binary hybrids. Morikawa et al. also indicates similar observation in his study on the preparation of a new class of polyimide silica hybrid films by sol-gel process. Similarly many researchers faced the problem in preparing the PI/titania hybrids as there was the aggregation of titania due to the faster condensation rate of Ti-OH groups as found in the literature [54-55].

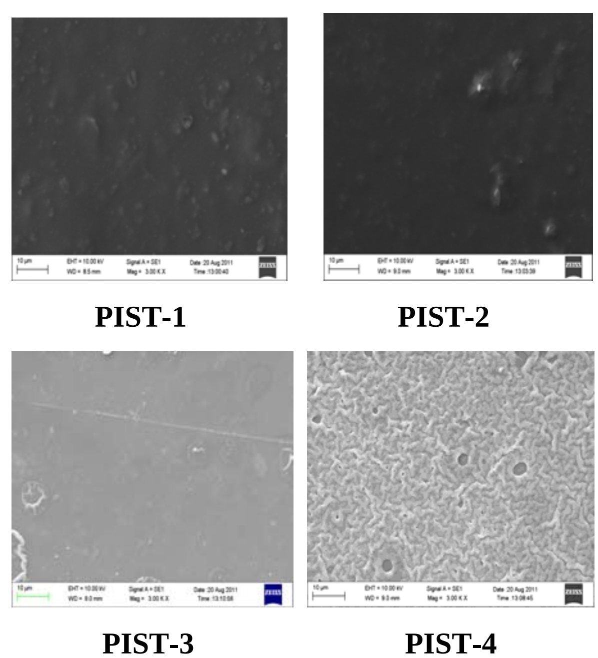

Fig. 5. SEM photographs of PIST-1, PIST-2, PIST-3, PIST-4

The interface adhesion can be improved by using suitable coupling agent to interlink between the two phases as depicted by Qiu et al. on the study of morphology and size control of inorganic particles in polyimide hybrids by using SiO_2-TiO_2 mixed oxide. The Fig.-PIST-2 represents the inhomogeneous dispersion as there is a little aggregation of the inorganic phases inside the polyimide matrix. The reason is due to the poor compatibility between the organic and inorganic phases. Figure-5 shows the dispersion of silica content only inside the polyimide matrix that might be about the incomplete interaction between the silica-titania inside the polyimide matrix. The formation of nanosized inorganic particles in case of PI/Silica/Titania shows two reasons. The first is about the silanol groups of lower reactivities that co-condense with Ti-OH on the surfaces of TiO_2 nanosized domains so as to prevent the accumulation of titania particles and the second is about the chelation between titania and PI main chains that enhances the adhesion between organic and inorganic phases.

4.6 Optical Properties of the PI/SiO_2/TiO_2 hybrids

The UV-Visible spectra of the PI and PI/SiO_2/TiO_2 are shown in the Fig.-6. It can be seen that with the increase in inorganic content, the absorption band moves towards longer wavelength and can be improved greatly by the addition of inorganic content. This is because by the adjustment of TiO_2 content[56] inside the polyimide hybrid composites. It can be seen that the transparency of PI/SiO_2 hybrid films decreases with the increasing in silica content[57] but can be improved by the addition of coupling agent (APTES).

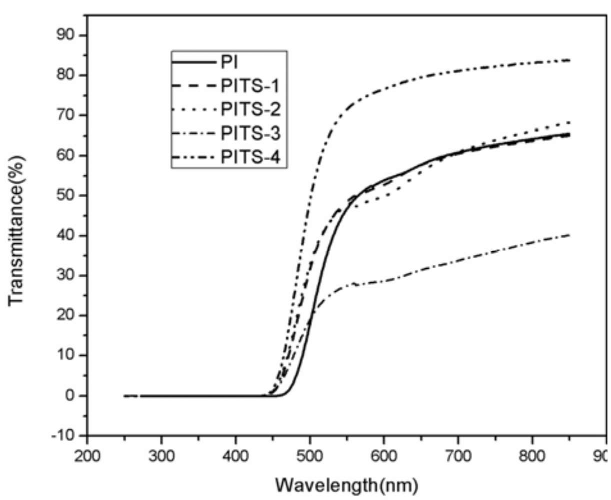

Fig. 6. UV spectroscopy of [PI ,PITS-1,PITS-2,PITS-3, PITS-4

The APTES hydrolyses to form silanol groups that can polycondense with the silanol groups of silicic acid oligomer and the amine group of APTES can react with PAA, the PI precursor. Compared with pure PI, the hybrid films have stronger absorption in visible region due to the TiO_2 content in the hybrids. The transmittance of PI/SiO_2/TiO_2 increases in the visible region in comparison to pure PI.

5. Conclusion

The PI/SiO_2/TiO_2 nanohybrids was successfully prepared from $TiCl_4$ and silicic acid using sol-gel method. By adjusting the silica and titania content, the size and distribution of the inorganic particles in PI matrix can be controlled. The bathochromic shift was observed for the hybrid due to the incorporation of titania and silica in the material and also increase in the glass transition temperature and degradation temperature proved its thermal stability. The control of the nanofiller addition can increase the mechanical strength which can be studied further. The obtained hybrid material may have potential applications in optoelectronic devices.

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