

Polyimide-Silica Nanocomposite Films Derived from their Precursors Blends

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ABSTRACT: A new method to synthesize Nanocomposite films of Polyimide/silica from the precursor solutions of polyimide and silica has been presented. It uses silica-generating Alkoxysilane, Tetraethoxysilane (TEOS) as precursor solution for generation of silica moiety within the Polyimide matrix in ultralow concentrations, which are in general, treated as neglected concentrations.

In comparison to Neat Polyimide, PI/SiO₂ Nanocomposite films showed improved mechanical properties and lower water sorption properties when ultralow concentrations (10⁻¹%, 10⁻²%, 10⁻³%, 10⁻⁴%, 10⁻⁵ %) of TEOS was used.

KEYWORDS: Polyimide, Blends, Nanocomposites, Alkoxysilane, Precursors, Sorption

I. INTRODUCTION

Polyimides (PI) are extensively used in microelectronics and aerospace industries owing to their excellent thermal, mechanical, and dielectric properties [11]. However, PIs exhibit relatively high value of water absorption and the coefficient of thermal expansion, which can limit their application in the field of electronics. Nanocomposites from PIs and silica offering favorable properties of the both are therefore in great demand and further improvement in these can be achieved by bringing the dispersion of inorganic materials to nanolevel in the matrix.

The compatibility between PIs and Silica generated in the sol-gel process using different tetraalkoxy silane in the composites, however, is not as good as expected because of weak interaction between the pure organic and inorganic phases [12]. Tendency of the silica network to agglomerates into large particles at higher silica loading ultimately leads to phase separation. Since the morphology of two phase systems affects the mechanical properties of polymer hybrids, attempts have been made to improve the compatibility between PIs and silica by increasing interfacial interactions. Wang et al. [13,14], Schrotter et al. [15], Chen and Iroh [16], Xenopoulos et al. [17], Musto et al. [18], and Chand et al. [19] have used different organosilanes with tetraalkoxysilane to produce silica network in the PI matrix. The organic groups present on these silanes, for example, aminophenyl-trimethoxysilane, aminopropyl-trimethoxysilane, diaminophenyltetramethyl-disiloxane, glycidylxy-propyltrimethoxysilane, aminopropylmethyl-diethoxysilane, and diaminopropyltetramethyl-disiloxane, are supposed to interact with organic PAA chain and alkoxy groups during the sol-gel process become the part of the silica network.

The reaction of the hydroxyl groups on the polymer chain, however, is slow with the alkoxy groups of TEOS and in the sol-gel process usually a physical bonding between the matrix and the silica network can be achieved. Also the Si-O-C bonds formed by the reaction of hydroxyl groups on the polymer chain and the alkoxy groups from the silane during the sol-gel process are considered weak.

Organic-inorganic hybrids, or Nanocomposites, have been proved as new advanced materials because they combine the advantages of organic components [e.g., flexibility, low dielectric constant (ϵ), and processability] and inorganic components (e.g., rigidity, strength, durability, and thermal stability) [1-11]. The enhanced properties of these hybrids mainly arise due to two reasons. First, the discrete inorganic phases, smaller than 100 nm, provide a very large interfacial area between the organic phase and inorganic phase and correspondingly cause the enhancement of the macroscopic properties of hybrids. Secondly, nanocomposites having molecular level of dispersion can result in hybrid polymers with specific properties [12]. Possessing versatile properties (especially dielectric and mechano-thermal properties) and its usage in a wide range of applications, polyimide (PIs) have been extensively investigated as matrices

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for hybrids in the search for novel materials for microelectronics and engineering. On the other hand, silica has been considered an ideal separated domain component in hybrids for improving the thermal and mechanical properties of materials [13]. The combination of nanoscale inorganic moieties with organic polymers has a high potential for future applications and has therefore attracted a lot of attention during the last years [14,15]

The prevention of phase separation and the control of morphology are the major factors in the development of Organic-Inorganic hybrid materials. In recent researches, the sol-gel method is widely adopted to control the morphology of the resulting hybrid material, and the use of compatibilizers to enhance the interfacial interaction between the two phases.

In the present work, here we report a study on the mechanical, morphological and water sorption properties of Polyimide-silica Nanocomposite films derived from their precursor blends.

These Nanocomposite thin films were prepared by using the precursor blend obtained from Tetraethoxysilane (TEOS) as a silica-generating precursor in relatively lower concentrations (which are generally treated as neglected concentrations) with PAA (Poly amic acid) which is a precursor to Polyimide (PI). In the present study we are thereby trying to focus on the synergism in macroscopic properties due to micro level modification by creation of nanophase structures, which are acting as functional synergist in nanodomains. The resultant properties are imbibed through inter-nanodomain manifestations.

The resulted precursor's blends were casted on glass substrate and subjected to necessary thermal treatment. The Morphological, Mechanical and Water sorption properties of the resultant thin Nanocomposite films were examined. We expected an efficient method for preparing Polyimide-Silica Nanocomposite films by blending ultralow concentrations of Tetraethoxysilane with PI for better-combined performance reflected in their macroscopic properties (here mechanical, morphological and water sorption properties are reported) .

II. EXPERIMENTAL

Materials

Tetraethoxysilane (TEOS)-99% pure, procured from Lancaster, USA was used as Silica generating precursor and was used as received.

Poly(amic acid)-PAA-a condensation product of Pyromellitic dianhydride (PMDA) and Oxydianiline (ODA) marketed as ABRON S-10 was procured from M/s ABR Organics Ltd., Hyderabad, India with 11.44% solid content in Dimethylacetamide (DMAc) with an inherent viscosity of 1.56 dl/g at 25°C and was used without further purification.

AR grade THF, Supplied by Merck, INDIA was used as co-solvent for the preparation of precursor solution.

AR grade Methanol, Supplied by Merck, INDIA was used as solvent for the removal of DMAc from the Nanocomposite films prepared for water sorption analysis.

Preparation of Polyimide-Silica Thin Nanocomposite Films

The Silica generating precursor solutions were prepared by adding TEOS in THF in different calculated w/w compositions.

Preparation of Polyimide-Silica Nanocomposite blends: The blends of different compositions were obtained by blending PAA with the Silica generating precursor solution. The relative amount of solution used was calculated to give SiO₂ content varying from 10⁻⁵ % to 20 wt.%.

The Nanocomposite films were obtained by casting of the prepared blends on glass plates and dried at 70°C over 18 Hrs for the evaporation of solvent. These films were then subjected to thermal treatment at 100°C, 150°C, 200°C, 250°C and 300°C for 15 minutes each and finally cured at 350°C for 2 Hrs. As a reference, Neat PI film was prepared in conditions identical to that of Nanocomposite films. The films are designated as PS1(Neat PI), PS2(3%), PS3(10%), PS4(10⁻¹%), PS5(10⁻⁵%) .

III. CHARACTERIZATION

1.AFM (Atomic Force Microscopy) analysis was performed on the cured thin films (appx. 25 micron thickness) using Nanoscope III, Digital Instruments, working in contact mode. The instrument is situated at CSR, IUC-DAE, Indore, INDIA where these samples were analyzed

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2. Mechanical Analysis of samples was performed on UTM (LR100K/LLOYDS, UK). This equipment is available at CIPET, Bhopal, INDIA where the analysis was carried out.

3. Water sorption Analysis: The water Sorption behavior was analyzed using ASTM D570. Samples were dried at 100°C for 1 hr. and dipped in methanol to leach out residual solvent (DMAc). These samples were dried at 120°C for 2 hrs and then dipped in 100 ml of water. The water uptake at different intervals of time till the equilibrium condition were determined by taking the weight of the samples using Perkin-Elmer's Microbalance (Model-AD-4) having accuracy up to 1 microgram.

The water sorption was calculated as per the formula:

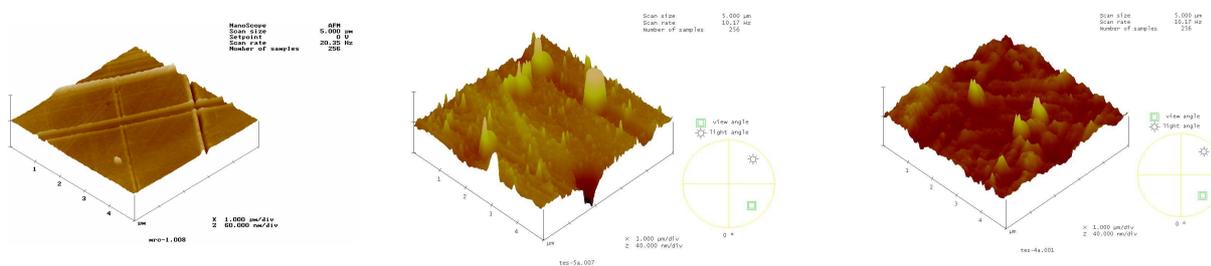
$$\text{Water Uptake (\%)} = \frac{W_0 - W_1}{W_1} \times 100$$

Where, W_1 is initial weight and W_0 is final weight

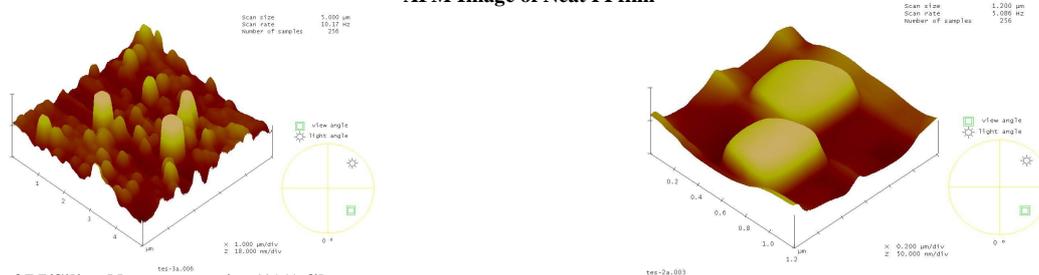
IV. RESULTS AND DISCUSSION

Morphological properties

The AFM results are given in fig. 1. The AFM analysis revealed that in higher concentrations of Silica in the PI matrix, a greater extent of aggregation of particles was observed in comparison to that visualized in low to ultralow concentrations of Silica used. This may be due to inappropriate and heterogeneous dispersion of the silica moieties in the PI matrix. When concentrations of silica are relatively higher, the inorganic moieties tend to coalesce to form clusters of bigger size approximately of 200-300 nm. While with lower concentrations of silica, the size of particles reduced up to 80-100 nm with a better dispersion of the particles within the PI matrix. This can be summarized that the incorporation of silica in lower concentrations results in the reduced domain sized in-situ generated silica moiety, which results in better dispersion as well as improved interfacial interaction of PI chains with the inorganic component within the PI matrix.



AFM Image of Neat PI film



AFM Image of PI/Silica Nanocomposite (1%) film

AFM Image of PI/Silica Nanocomposite (20%) film

Mechanical properties

The results of mechanical properties are given in fig.2. The mechanical properties of a glassy polymeric system depend on the crystallinity introduced into the chains, orientation of the macromolecular segments, and the amount of cross-linking between the macromolecular units. When stress is applied to such materials, the weakest link, i.e., the non-bonded interchain interaction, deforms much easier than the strong covalent bonds along the individual chains. Thus the network of non-bonded interchain interactions plays a crucial role in determining the magnitude of the strength in that particular polymer. The presence of the crystalline region can lead the polymer to behave like a rigid rod while the

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amorphous region will compel the polymeric chain to act as an elastomer. The increase in the crystalline region can act as a stress raiser and thereby weakens the polymer network to cause premature failure [16, 17, and 18]. The tensile strength and elongation at break of the PI/SiO₂ Nanocomposite film are shown in Figure 2. It has been observed that, when the silica concentrations was less than 10 wt %, both the tensile strength and the elongation at break increased in comparison to that of pure PI. When the silica concentrations was 10 wt % and above, both the tensile strength and the elongation at break has decreased. Nanocomposite with silica nanodomains in ultralow concentrations exhibited drastically improved mechanical properties, and this could be explained in two ways: (1) nanometer-size silica dispersed relatively more homogenous throughout the PI matrix, and (2) PI chains strongly interacted with silica or silanol moieties through hydrogen bonding and consequently became entrapped with silica particles [19]. The decrease in tensile strength and elongation with the higher concentrations of silica moieties should be due to the formation of Si-O-Si networks in the hybrids. In comparison with the PI matrix, the fragile Si-O-Si networks possessed much weaker tensile strength and lower elongation properties. These properties imparted intrinsically decreased mechanical performance in the resultant thin nanocomposite films, especially in the samples with higher SiO₂ concentrations.

Water Sorption Properties

The water sorption behavior of the PI/Silica Nanocomposite films was studied and results are given in Table-1. The water sorption behavior as obtained indicated lower values of water sorption in case of ultralow to low concentrations of PI/Silica nanocomposite films compared to the values that obtained for Neat PI. In case of higher concentrations of silica content, such as 20%, the value shows a steep increase of 4.5% compared to the Neat PI value which is 2.26%. While when we considered the lower concentration case the values goes down up to 1.48%. This can be explained on the basis of synergistic improvement in the core properties of Polyimide because of smaller compact nanosize silica domain dispersion within the PI matrix which resulted in greater interfacial interaction and dense packing fraction. In each nanocomposite film, water uptake was lower than that of neat PI. Lower water sorption in nanocomposites may be attributed to the presence of silica moieties as nanoparticles in the interstitial sites or in the available free volume of polymeric matrix, thereby filling the free space available for water molecules to reside [20].

S. No.	Concentration	Water Sorption (%)
1	PS1 (Neat PI)	2.26 %
2	20 %	4.5 %
3	PS3 (10 %)	3.45 %
4	PS4 (10 ⁻¹ %)	1.59 %
5	10 ⁻² %	1.56 %
6	10 ⁻³ %	1.93 %
7	10 ⁻⁴ %	1.56 %
8	PS5 (10 ⁻⁵ %)	1.48 %

Table-1 Water sorption (%) of Neat PI film and PI/SiO₂ thin Nanocomposite films at Equilibrium Condition

V. CONCLUSION

The morphological, water sorption and mechanical properties of PI/SiO₂ thin nanocomposite films prepared by using TEOS as silica precursor were studied and their relationships to silica contents were investigated. Lower Concentrations (Ultralow to low concentrations) has been proven to be an effective way for preventing phase separation between PI and silica moieties. By controlled incorporation of silica content, the control in size and homogenous distribution of the inorganic particles or silica nanodomain in PI matrix can be improved. Consequently, the properties of the resultant PI/SiO₂ thin nanocomposite films such as transparency, CTE, thermal decomposition temperature, tensile strength, water sorption behaviour, etc. can be easily modulated resulting in their effective usage in wide spectrum of applications in nanotechnology.

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