

PVDF: PI nano composite films: mechanical, FT-IR, XRD, AFM and hydraulic study

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Abstract In today's era of modern technology study of nano composite thin films are of immense importance. Unmodified PI, PVDF and PVDF incorporated PI thin films were prepared by spin coater unit using solution cast technique. PVDF was incorporated in variable lower concentrations in PI matrix at its precursor stage i.e. PAA. Thereafter, degree of crystallinity, crystalline nano particle size was evaluated using XRD and AFM technique. FT-IR was used to study the physical incorporation of PVDF particles within the PI matrix. Further, these results were used to study the microhardness, tensile and hydraulic behaviour. However, PVDF incorporated PI nano composite thin films contain overall better property in form of increased microhardness, tensile strength and less water absorption with improved morphology in comparison to unmodified film and 0.5 wt % nano composite film shows synergistic enhancement.

Keywords PI · PVDF · XRD · AFM · FT-IR · Microhardness · Tensile behaviour · Morphology

Introduction

Conventional multifunctional materials, such as fibre-reinforced or filled polymers, require a trade-off between various mechanical and physical properties, cost and

processability. However, combinations of properties derived at the nano scale provide opportunity to circumvent these traditional trade-offs. The transition from micro-particles to nano particles leads to a number of changes in physical properties [1–3]. Additionally, the fact that nano particles have dimensions below the critical wavelength of light can render them transparent, which has implications for part aesthetics. Nano technology, a route to define the concept of traditional science has now become a focal point towards the advancement of many areas in modern science and technology. Aromatic polyimide (PI), a condensation product from the reaction between pyromellitic dianhydride finds use in myriad of technical and industrial fields such as dielectric materials for microelectronics, high temperature adhesives, photoresists, non linear optical materials, membrane for gas separation, atomic oxygen resistant polymers for low earth orbit spacecrafts and microelectronics. These applications arise as polyimides are associated with excellent mechanical properties, less relative permittivity, high breakdown voltage, low losses over a wide range of frequency, good planarization, good processability, wear resistance, inertness to solvents, good adhesion properties, low thermal expansion, good hydrolytic stability and long term stability [4–8].

Fluoropolymers, like poly (vinylidene fluoride) (PVDF) have been used in important specialized applications. PVDF has good weather resistance and its mechanical properties are excellent [9, 10]. PVDF is a semi-crystalline polymer which has drawn both scientific and technological attention because of the useful pyroelectric [11] and piezoelectric [12] properties. It is also one of the rare polymer exhibit diverse crystalline forms, having at least five phases known as α , β , γ , δ and ϵ [13–15]. The objective of the present work is in situ generation of PVDF crystalline particles within the polyimide matrix to prepare

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nano composite thin films and to study the effect of nano crystalline particles on the microhardness, mechanical and hydraulic performance of developed composite thin films so that they can be used in variety of applications mainly as multifunctional characteristic flexible solar cell and storage device for microelectronics.

Experimental

Materials used

Polyamic acid [Benzene,1,2,4,5-tetracarboxylic acid (PMDA), 1,2,4,5-dianhydride, and 4,4'-diaminodiphenyl ether (ODA)] having 42,000 M_w was supplied by ABR, Organics Ltd. Hyderabad, India. PVDF with 140,000 M_w , in powder form was procured from Aldrich, USA and used as received due to their high purity (over 99%). Double distilled water was used for hydraulic characterization.

Preparation of films

Preparation of blends The known mass of polyamic acid solution and the calculated quantity of PVDF were added so that the films having ultimate desired concentration of 1.5, 1, 0.5, 0.1 wt.% of PVDF within the PI matrix are obtained which have been designated as PIF-4, PIF-3, PIF-2 and PIF-1, respectively. The unmodified polyimide and poly (vinylidene fluoride) films were designated as PI and PVDF. The blends were stirred for 1 h on a magnetic stirrer for the mixing of PVDF within the PI matrix.

Preparation of composite films The blends of different composition were spread evenly over clean and dry glass plates with the help of a glass rod in a dust and moisture free environment. The glass plate was then kept inside the incubator at 70 °C for 12 h to ensure the slow imidization of dimethylacetamide (DMAc), which is present within the PAA. Oven was used to maintain the temperature curing profile from 100 °C up to 350 °C which involves the time profile of 30 min after every 50°C up to 300 °C and at 350 °C temperature was maintained for 2 h to ensure the crosslinking between the PI matrix and PVDF crystalline nano particles. Thereafter, oven was made to cool down to room temperature and films were removed from the glass plates. This yields specimen in the form of composite thin films of 20.0001 ± 2 micron. A known quantity of this homogenous solution was poured in glass mould, which was built in form of pellets block. Thus, the yield specimens were of 1 mm thick especially for microhardness characterization. For measurement of film thickness micrometer gauge having 0.0001 least count was used.

Characterization

FT-IR

The Fourier Transform Infrared Spectrometry (FT-IR) of unmodified PI, PVDF and PIF-2 thin films were obtained using Perkin Elmer FTIR Spectroscopy BX instrument.

XRD

X-ray diffraction (XRD) technique has been utilized to detect changes in crystalline and amorphous regions along with the degree of crystallinity and nano crystalline particle size of unmodified and composite thin films. Specimens were kept in aluminium sample holder in such a way that upper surface is smooth and was exposed to X-rays in vertical goniometry assembly. The scan was taken between (10–80°) 2θ with scanning speed of 20° 2θ per min, the operating target voltage was 35 kV, with a current of 20 mA and radiation used is FeK alpha with wave length of 1.93735 Å on Rigaku Rotating anode mode RU-H3R (18 kW), X-ray powder diffractometer and to evaluate the crystalline size K_α line of copper ($\lambda=1.5418$ Å) irradiation source was used

AFM

AFM topography of unmodified PI and PIF films were imaged using (DIAFM-4 instrument) in tapping mode. Generally AFM works on two modes contact mode and tapping, however, due to the softness of the polymeric blends, AFM topography was taken out in tapping mode, which is more suitable for soft polymeric materials.

Microhardness measurement

Microhardness measurements on unmodified PI and PIF films were carried out using Carl Zeiss NU₂ Universal Research Microscope model mph-160 with a Vickers diamond pyramidal indenter attached to it. The Vickers Hardness Number (H_v) was calculated using Morley [16] Eq. (1):

$$H_v = \frac{1.854 \times L}{d^2} \text{ (kg/mm}^2\text{)} \quad (1)$$

Where, L is the applied load and d is diagonal of indentation. Minimum five indentations were obtained at various loads and the average hardness number was calculated.

Mechanical test

Mechanical characterizations of the unmodified PI and PIF films were carried out according to ASTM test method no.

D-638. Crosshead speed was maintained at 5 mm/min at room temperature. The samples were conditioned at 110 °C for 24 h in air before the testing. The mechanical tests were conducted at room temperature on an Universal Testing machine (Model No. 4302). The tests were made on 1 × 15 cm² size samples. The crosshead speed (initial strain rate) was 5 mm/min and grip length 40 mm. The tensile strength, modulus and elongation at break were measured using the stress–strain curves.

Hydraulic test

The prepared unmodified PI and PIF films were dried at 110 °C for 2 h and then accurately weighed films were dipped in double distilled water. The water absorption at different interval of time at room temperature (25 °C) was

recorded till the equilibrium was obtained. The percentage of water absorption was calculated by using the Eq. (2):

$$\text{Solvent absorption (\%)} = \frac{W_f - W_i}{W_i} \times 100 \quad (2)$$

Where,

W_i initial weight of the film (weight after removal of water)

W_f final weight of the film (after water absorption)

Result and discussion

FT-IR analysis

Fourier Transform Infrared Spectrometry (FT-IR) has been utilized to analyse the physical incorporation of PVDF

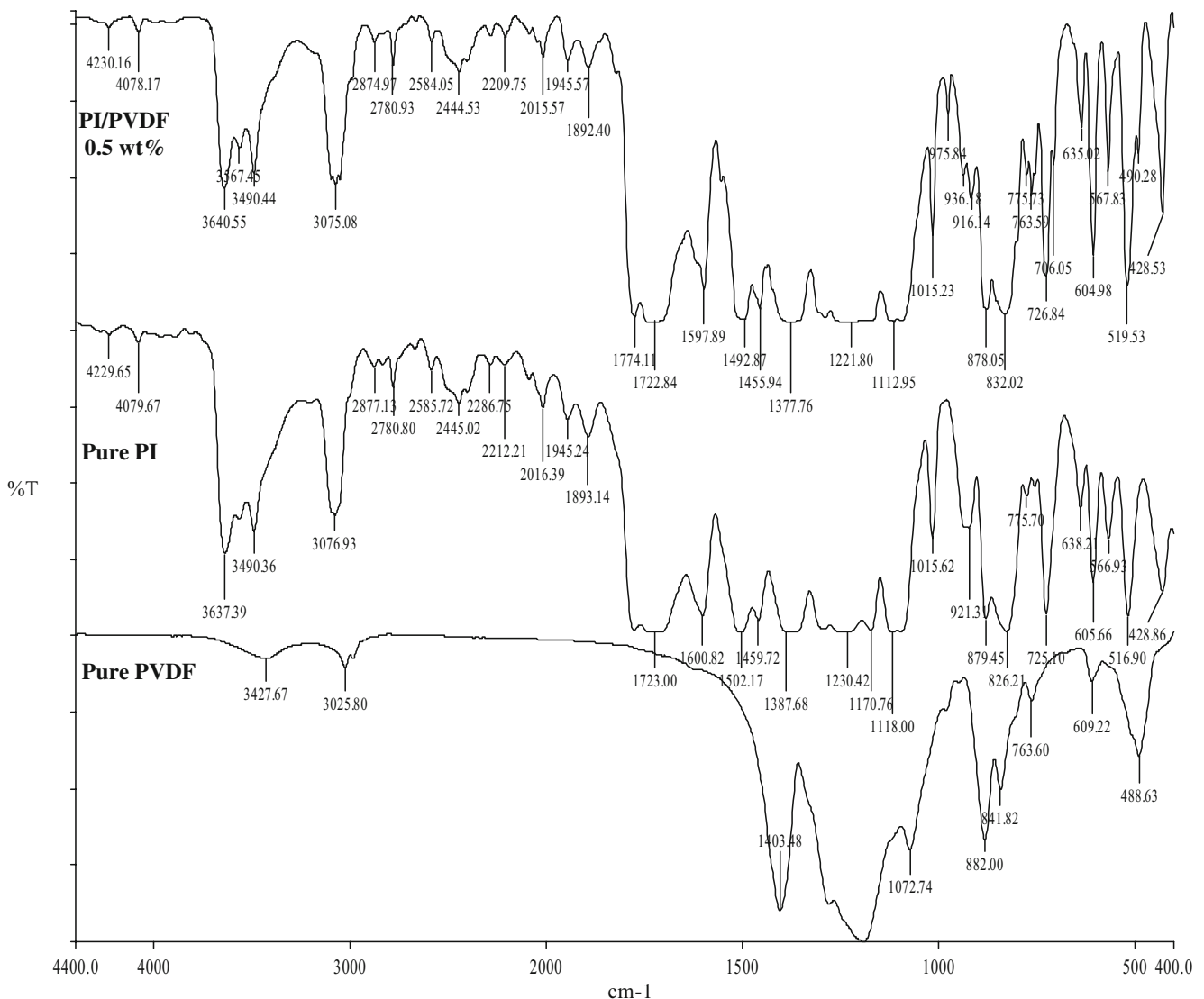


Fig. 1 FT-IR spectrum of unmodified PI, PVDF and PVDF incorporated PI films i.e. PIF-2

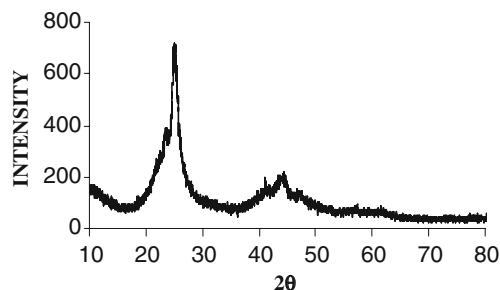


Fig. 2 XRD graph for PIF-2 film

within the PI. Figure 1 shows the FT-IR spectrum of unmodified PVDF, PI and 0.5 wt.% PVDF incorporated PI films. A close examination of physical appearance of PIF film incorporated in low concentration seems to have a uniform and smooth surface. On observing the FT-IR spectrum of PIF film of 0.5 wt.% it is clear that the characteristic peaks of PI and PVDF films are present in PIF which shows the blending of two polymers. The characteristic absorption band of pure PVDF α -phase at $488.63\text{--}1,072.74\text{ cm}^{-1}$ and β -phase at $841.82\text{--}1,403\text{ cm}^{-1}$ are observable. Absorption band of pure PI clearly indicates the presence of aromatic compound possibly the phenoxy or amino substituent. However, the spectra of PIF film for 0.5 wt.%, shows the presence of α - and β -phase along with the aromatic ester – possibly polyfluoro substituent ($1,005\text{--}1,780\text{ cm}^{-1}$). The absorption band appearing at $832.02\text{--}878.05\text{ cm}^{-1}$ is assigned to the characteristic frequency of vinylidene compound in PIF film i.e. 0.5 wt.%. It is clear that the stretching frequency at $1,723\text{ cm}^{-1}$ which corresponds to C=O of pure PI, is shifted to $1,774\text{ cm}^{-1}$ in the PIF film. This shift observed in carbonyl stretching frequencies of blends when compared to pure PI due to specific interaction between the unsaturated carbonyl groups of PI and the CH_2 groups of PVDF indicates the formation of composite. Moreover, the crystalline β -phase of PVDF at 878.05 cm^{-1} in PIF film is observed.

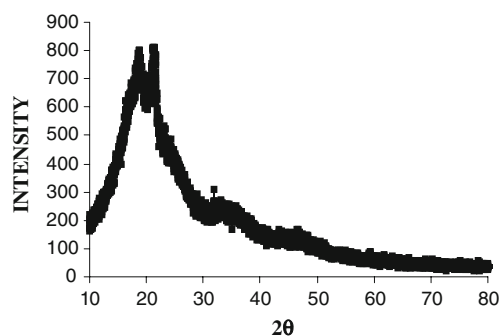


Fig. 3 XRD graph for pure PI film

Table 1 Calculated value of crystallinity for pure PI and PIF films

S. no.	Sample designation	Calculated crystallinity index (X_c)
1.	Pure PI	0.12
2.	PIF-1	3.12
3.	PIF-2	3.96
4.	PIF-3	2.98
5.	PIF-4	0.56

XRD analysis

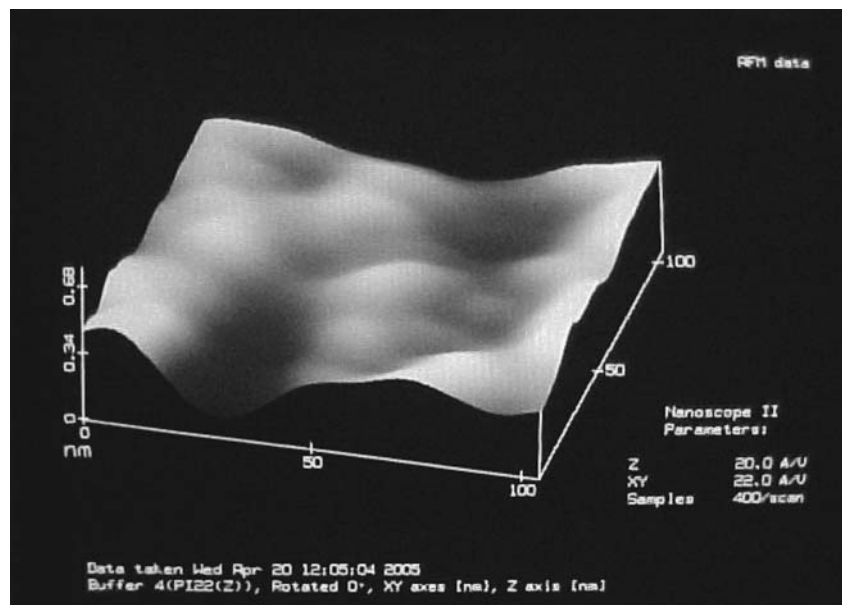
X-Ray diffraction technique was used to characterize the degree of crystallinity and size of crystalline particle. Degree of crystallinity has been calculated on the assertion that increasing amorphousness tends to broaden the intensity vs line width peak (Fig. 3) where as increase in degree of crystallinity shows narrow sharp peak (Fig. 2). However, degree of crystallinity can also be estimated by comparing the intensity and width of lines. The morphology of most of the polymers is semicrystalline crystalline, which is due to folding and stacking of the polymer chains. The crystallization depends on the degree of miscibility and mobility of crystallisable and non-crystallizable components in the blend specimens. The intensity versus 2θ scans were obtained for unmodified PI and PVDF/PI composite thin films (Figs. 2 and 3). For obtaining crystallinity index from XRD patterns of samples, the approach of Hermans and Weidinger [17] has been utilized. The scan is resolved in “crystalline peaks” and “amorphous peak” and the “background” and the following assumptions are made:

1. The total scattering from the sample is divided between crystalline peaks from the “crystallites” amorphous peaks from the remaining “amorphous regions.”
2. The total scattering from the sample is that included in the resolved crystalline and amorphous regions.
3. The relative areas of the “crystalline” peak and the “amorphous” peak are respectively proportional to the number of electrons (and thus mass) in the “crystalline” and the “amorphous” regions.

Table 2. Particle size of pure PI and PIF films from XRD analysis

S. no.	Sample designations	D (\AA) nm
1.	Pure PI	Particles not present
2.	PIF-1	2.87
3.	PIF-2	1.62
4.	PIF-3	3.98
5.	PIF-4	Agglomeration starts

Fig. 4 AFM topographic image of PVDF incorporated PI film i.e. PIF -2



With these assumptions, the crystallinity index (X_c) is calculated (Table 1) for each sample from the resolved peak areas [18] using the Eq. (3),

$$X_c = \frac{A(C_r)}{A(C_r) + KA(A_m)} \quad (3)$$

Where, $A(C_r)$ is the area of crystalline peak, $A(A_m)$ is the area of amorphous peak, and K is constant, for comparison K is set to unity.

To evaluate the nano crystalline particle size of PVDF within the PI matrix the finite three-dimension crystal lattice diffracts X-rays in a manner analogous to the reflection of visible light from a ruled grating was used. When the particle size is of the order of the wavelength of incident beam, the diffraction beam becomes diffused. As crystals decreases in size, the diffraction beam becomes more and more diffused until it is lost in the general background as for amorphous material. Thus the

Fig. 5 AFM topographic image of pure PI film

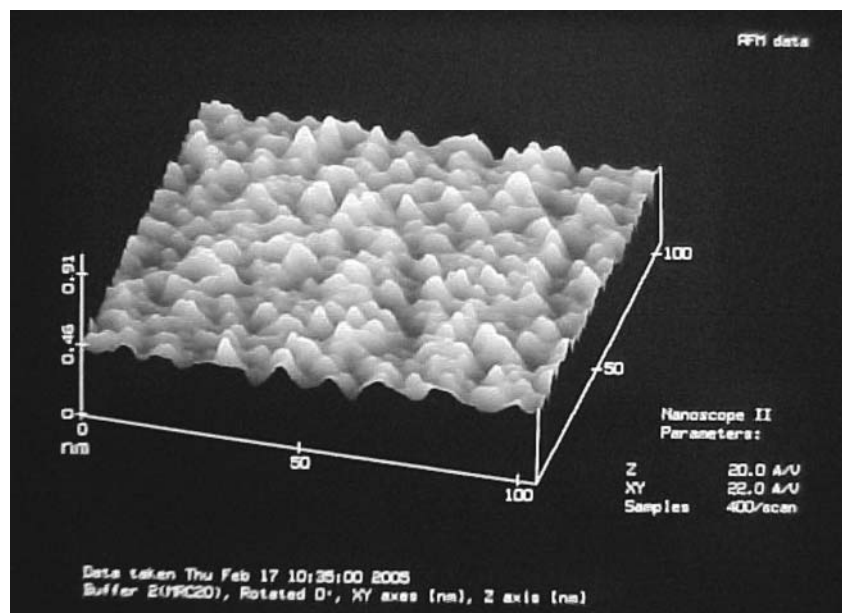
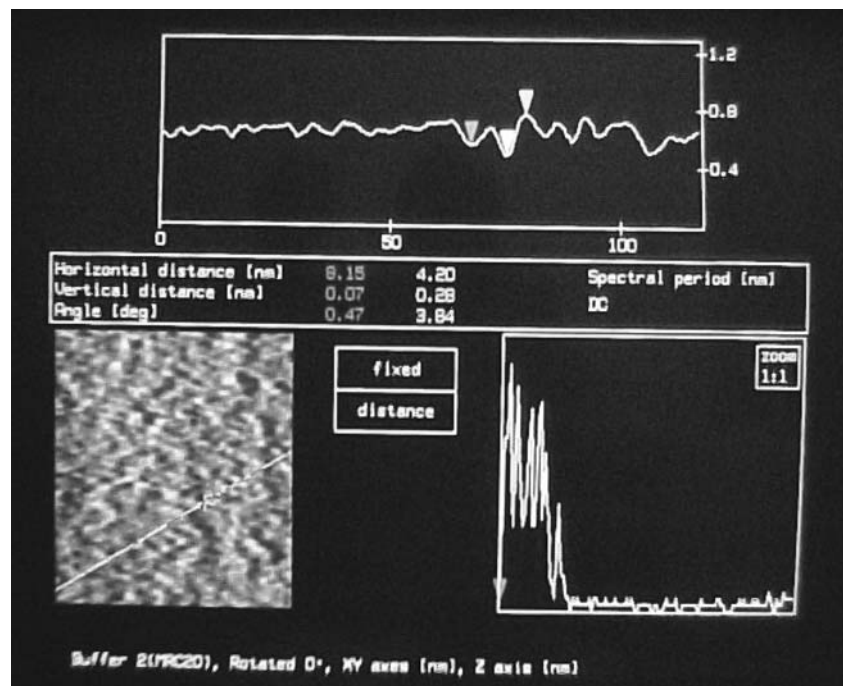


Fig. 6 Particle size analysis of PVDF incorporated PI film i.e. PIF-2 using AFM technique



width of the X-ray diffraction line is able to give crystalline size. The relationship between the crystalline size and diffraction ray line broadening is given by Scherrer [19] Eq. (4):

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (4)$$

Where, K is constant which depends on the crystalline and diffractometer setup, λ = wavelength of monochromatic radiation, β = full width at half maxima (FWHM), θ = diffraction angle or Bragg angle.

The value of $K=0.9$ and $\lambda=1.518 \text{ \AA}$, which are equipment parameters and the value of β and θ can be obtained from the diffraction pattern. The calculated value for nano crystalline particle size for each composite film is reported in Table 2.

AFM analysis

Atomic force microscopy (AFM) was used to study the surface morphology of prepared composite thin films. Figure 4 shows the 3D, AFM topographic image of the unmodified PI film. The 3D, AFM topographic image (Fig. 5) for (PIF-2) shows greater degree of crystallinity along with uniform distribution of nano crystalline particles. Whereas, Fig. 6 shows the incorporated crystalline particle size analysis of PVDF within the PI matrix for (PIF-2) film. Polymer micro and nano structures are fundamental to a number of modern technological applications including polymer nano composite. Nano structure

can alter the morphological feature of polymeric composite to a great extent which generally affects the mechanical and hydraulic properties.

In this study, the surface crystalline morphology of PVDF and its miscibility with PI were studied using atomic

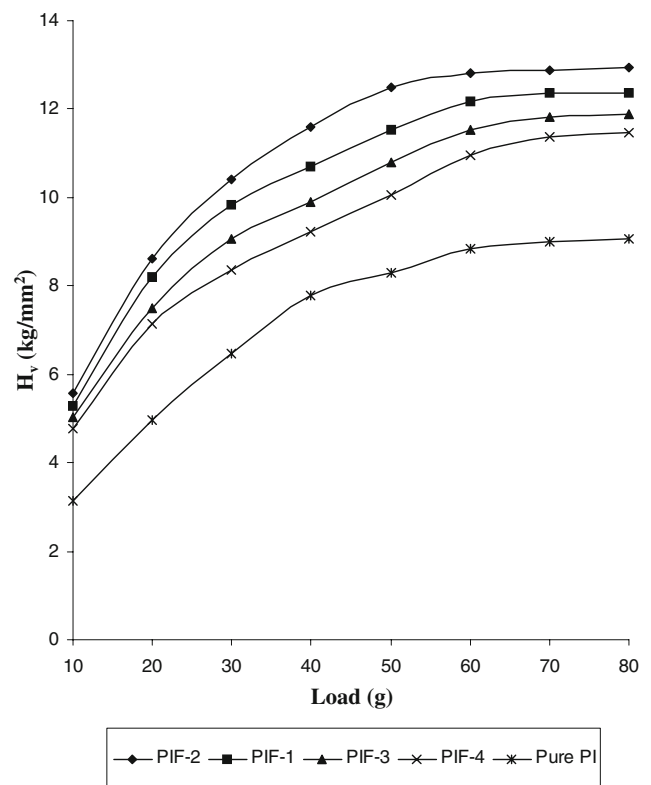


Fig. 7 H_v vs load graph of pure PI and PIF nano composite films

Table 3 Different calculated values of (*n*) for pure PI and PIF films in the two load regions are shown

Samples designation	Slope	
	(<i>n</i>) low load	(<i>n</i>) high load
Pure PI	2.67	2.22
PIF-1	3.2	2.01
PIF-2	3.34	2.00
PIF-3	2.98	2.15
PIF-4	2.82	2.18

force microscopy. The formation of blend using these polymers can be attributed to a development of good polymeric material with improved morphology for high temperature resistive material.

The surface structure of polymer blend has attracted much interest because of the practical importance of the associated functional properties. It has been revealed that the surface structure of nano materials is clearly different from that in the bulk, mainly depending on the difference in the surface free energy of each component. This result is significant in the light of the comprehensive difference in properties between the crystalline and amorphous phase of a semi crystalline polymer. The nano structure of PVDF within the matrix of PI is observable by AFM; the observation can give detailed information on the surface morphological change due to the interaction between the two polymers when a blend is composed of semi-crystalline polymer as one component. The most significant outcome of the proposed work is better miscibility with greater degree of crystalline crosslinking of PVDF within the PI matrix.

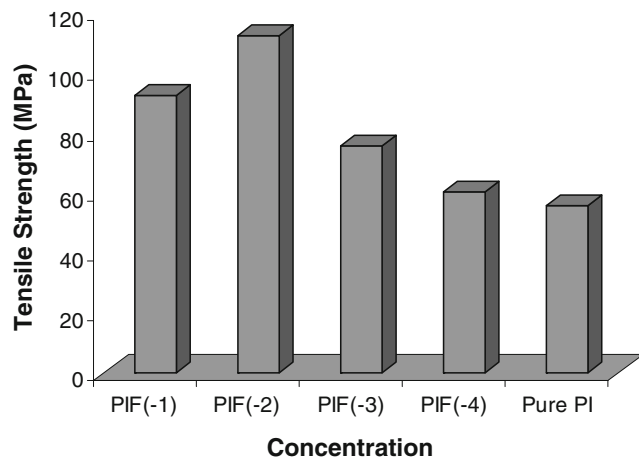


Fig. 8 Graph of tensile strength for pure PI and PIF films

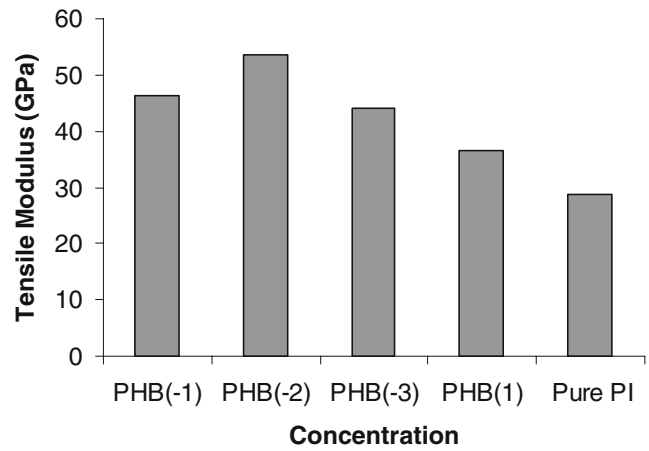


Fig. 9 Graph of tensile modulus for pure PI and PIF films

Microrhardness analysis

Microhardness testing has been utilized to obtain information on structural features and mechanical property changes for nano composite thin films. Further, the important aspect of the microhardness testing of polymers at low loads is that whether the hardness number is dependent or independent of the load. It is with this view the effect of load on the microhardness of pure PI and PVDF/PI nano composite thin films along with the mechanical performance i.e. tensile strength, tensile modulus and elongation have been studied. Figure 7 shows variation of Vickers hardness number (H_v), as a function of applied load (L), for unmodified PI and PI/PVDF nano composite films with varying wt.%. The increase in the value of H_v , as the load increases can be explained on the basis of strain hardening phenomenon in polymers [20, 21]. There are micromodes of deformation in the polymer chain. When sufficient numbers of micromodes become active, large-scale plastic deformation begins. As the load is increased, the specimen

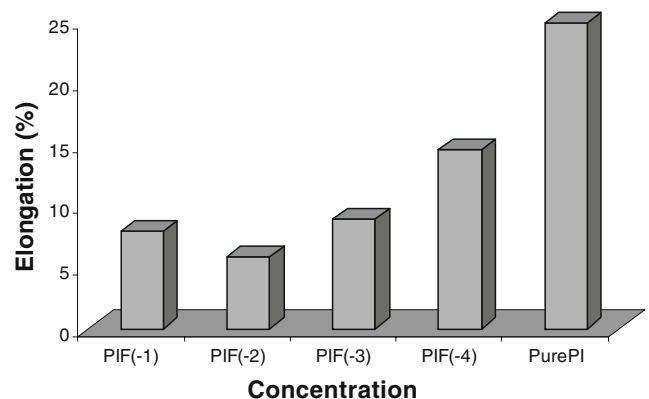


Fig. 10 Graph of elongation for pure PI and PIF films

Table 4 Hydraulic measurement of pure PI and PIF films

S. no.	Sample designation	Moisture absorption (%)		
		24 (h)	M α (h)	Average value
1.	Pure PI	4.11	4.32	4.23
2.	PIF-1	3.21	3.29	3.25
3.	PIF-2	1.10	1.40	1.20
4.	PIF-3	2.80	3.45	2.96
5.	PIF-4	4.00	4.08	4.04

is subjected to greater strain hardening and H_v is increased. The shape of H_v – load profile for this specimen is found to be curvilinear. Finally, when H_v tends to saturate the polymer specimen is fully strain hardened as no appreciable change in the value of H_v is observed. Initially when PVDF is blended with PAA by molecular root and heated upto 350 °C the semi crystalline PVDF gets incorporated within the PI matrix in form of nano crystalline material and gets crosslinked. Thus, this crosslinking of nano crystalline particles within the PI matrix increases the H_v value in comparison to unmodified PI and for 0.5 wt.% nano composite film, microhardness is found to be maximum along with greater degree of crystallinity as reported in Table 1.

Strain hardening index

The nature of load dependence of microhardness on the unmodified PI and PIF films can be studied using the Eq. (6):

$$L = ad^n \quad (5)$$

Taking logarithm on both sides of the Eq. (5), we have:

$$\text{Log}L = \log a + n \log d \quad (6)$$

Where L is load, d is the length of the diagonal, a is a constant representing load for unit dimension and (n) is the logarithm index number, which is the measure of strain hardening, obtained from the plots of $\log L$ versus $\log d$. The plots clearly recognise straight line with different slopes for low and high load regions. The value of (n), for PI and PIF films are listed in Table 3. The low load region ranges from 10 to 60 g and high region ranges from 70 to 100 g. It is evident from Meyer's law [15] that when H_v increases continuously with load then $n > 2$. The value of (n) approaches around 2 in the saturation load region at which H_v becomes independent of load. Therefore, in low load region, (n) is greater than 2. In most of the PIF films,

the value of (n) tends to be greater than 3 in low load region and nearly 2 in the high load region. In fact, the different values of n in the different load regions reflect the elastic and plastic characteristics of deformation.

Tensile behaviour

Mechanical properties of any polymeric system depend on the nano/macromolecular segments and amount of cross-linking between the macromolecular units. Tensile properties and tensile modulus is one of the important parameters along with elongation in mechanical properties. It is the key indicator of the stiffness or rigidity and quantifies the resistance of the material to mechanical deformation in the limit of infinitesimally small deformation. The results of various mechanical properties of unmodified PI and PIF films at 350 °C are shown from Figs. 8, 9, and 10. It can be inferred from the Fig. 8 that incorporation of PVDF at nano level in PI matrix has significantly affected the tensile properties. Tensile strength of PIF films are found to be greater than the unmodified PI films. This shows the influence of PVDF nano crystalline particle and cross-linking between them within the PI matrix. Maximum tensile strength is obtained for PIF film having 0.5 wt.%.

Hydraulic analysis

The moisture absorption characteristics of synthesized films have been evaluated by constructing water absorption isotherm, which involves immersion for 24 h and maximum 144 h. The presence of moisture can alter the entire properties. Physicochemical properties depend upon interaction between the filler and the matrix. Table 4 shows the hydraulic absorption of PI and PIF films. Minimum absorption is observed for 0.5 wt.% where the degree of crystallinity is greater along with crosslinking within the PI matrix which more eminent. Lower water absorption in case of PIF films may be attributed to the presence of nano crystalline particles as a modifier in PI matrix. Available free volume in polymeric matrix gets filled by PVDF nano crystalline particles and thus restricting the absorption of water molecules.

Conclusion

The FT-IR, XRD and AFM study helps us to evaluate the nano structure within the PIF films. However, evaluating the nano structure within the PIF films, the effect of nano particles in PI matrix has been analysed and result shows good conformity. PIF films have better mechanical properties along with hydraulic stability. PIF film having 0.5 wt.% of PVDF shows superiority in all respect. Thus these PIF

films can be used as high temperature ablative material for microelectronics with excellent mechanical properties.

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