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POLYIMIDE-EPOXY ALLOYS PREPARED VIA MICRO-MODIFICATION : WATER SORPTION AND DIFFUSION

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SUMMARY : A novel polyimide-epoxy or PI-EP alloys are prepared by the modification of polyamic acid in the concentration range of $1.54\text{x}10^{-6}$ to $1.54\text{x}10^{-2}$ mol/L. The methanol sorption for these alloys at 24 hrs and at equilibrium conditions are determined and the residual solvent in fully cyclized polyimides were calculated. The presence of the residual solvent is visualized in fully imidized polymer and a structure containing partly imidized amic acid moiety is proposed and their concentration (in percentage) is calculated. The water sorption for these alloys at 24 hrs and at equilibrium conditions and the values of the water diffusion coefficient are determined from absorption isotherms. The PI-EP alloys have shown comparatively lower water sorption and higher diffusion coefficient than the unmodified polyimide. The mechanistic aspects of water sorption and diffusion are discussed.

INTRODUCTION

In speciality class of polymers particularly high temperature resistant polyimide, water diffusion and sorption behaviour have been the subject of immense interest in both academic and industrial field. The water present in polyimide has been found to affect its inherent macroscopic properties and induce degradation of the dielectric properties and causes metal corrosion [1]. The polyimides are used in the fabrication of microelectronics devices due to their superior dielectric and mechanical properties coupled with excellent thermal stability and chemical resistance and its amenability to process in thin film configuration [2]. The major drawback of polyimides is their hygroscopic nature which results in the absorption of 1-5% of moisture [3]. The testimony of the significance attached to the transport and diffusion of moisture/water in polyimide film is that, the polyimide is the single class of polymer whose water sorption characteristics have been very extensively studied [4]. On one hand the comprehensive studies on water sorption has been undertaken and on the other end a vigorous effort has been made to synthesize the polyimides with water sorption as low as possible [5,6]. A new class of polyimide alloys

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has been developed at Macromolecular Research Centre, R.D.University, Jabalpur, India [7-11] which have exhibited lower water uptake while retaining their other excellent macroscopic properties. In the present paper the water sorption and diffusion of the polyimide-epoxy alloys prepared by the unique technique of in-situ generation of blend components via micromodification [8] have been investigated as such properties of these alloys have not been studied so far.

EXPERIMENTAL

Materials and Instruments used

Polyamic acid (PAA) - a condensation product of pyromellitic dianhydride (PMDA) and oxydianiline (ODA) was procured from M/s ABR Organics Ltd., Hyderabad, India and this product is marketed as ABRON S-10, which was a 10% solution in dimethyl acetamide (DMAC). The intrinsic viscosity of PAA was given as 1.5 dl/g by manufacturer but its intrinsic viscosity was found to be 0.95 dl/g when it was determined in the laboratory. The PAA was kept in an air tight container stored at low temperature (-2 to +3^{o} C). The micromodifier epoxy i.e.diglycidyl ether of bis phenol-A (designated as EP) was obtained from M/s Cibatul Co., Ltd., Mumbai, India. It has epoxy value 5.2 to 5.5 equiv./Kg. and its viscosity at 25^{o} C was 0.9 to 1.2 Pa.S. The reagent grade DMAC solvent was supplied by M/s CDH Laboratories, Mumbai, India. DMAC was purified by distillation in the presence of P_2O_5 and the fraction between 162^{o} C and 166^{o} C was collected and was always kept in a closed container.

The degree of imidization of all samples were determined by IR Spectroscopic technique. Spectra of PAA/polyimide films were recorded using Perkin Elmer's FTIR Spectrophotometer (model 1720 X).

Synthesis/Preparation

Calculated quantity of EP in DMAC was mixed in PAA solution at different concentration levels so as to result the PI-EP film of 50 micrometer thickness having varying concentration of EP, viz., $1.54\text{x}10^{-2}$, $1.54\text{x}10^{-3}$, $1.54\text{x}10^{-4}$, $1.54\text{x}10^{-5}$ and $1.54\text{x}10^{-6}$ mol/L of polyimide, and they are designated as PI-EP-2, PI-EP-3, PI-EP-4, PI-EP-5 and

PI-EP-6 respectively. The neat PI (i.e. without EP) is designated as PI-1. The quantity of the solvent in EP solution should be such that its addition to PAA should not affect solvent concentration substantially. PAA and EP solutions were mixed thoroughly and spread over a glass plate with the help of doctor's blade. For thermal imidization and as well as solvent removal the samples were heated in steps upto ultimate temperature of 350° C for 2 hrs. The samples were cooled to room temperature and removed from the glass plates.

Characterization

Degree of imidization

For the degree of the imidization a band ratio method was adopted wherein the area of symmetric carbonyl stretch at 1776 cm^{-1} was ratioed with area of reference aromatic vibration at 1012 cm^{-1} [12].

Alcohol uptake and outdiffusion of residual solvent

The samples were dried at 110 ° C for 1 hour and the dried samples of 2x2 cm^2size were dipped in 100 ml of methanol in a beaker for 48 hrs to enable leaching out the inadvertently present residual solvent (i.e. DMAC) in polyimide and its alloys. Residual solvent was leached out in methanol hence the weight difference before and after drying has given the amount of the residual solvent, which got removed by this outdiffusion method.

Water uptake

The samples were heated at 110° C for 2 hrs to remove the methanol and then dried samples were kept in 100 ml of double distilled water in a beaker. The water uptake at different intervals of time till the equilibrium conditions were recorded, at constant temperature (23° C). The weights were taken by the Perkin Elmer's microbalance (model AD-4) with accuracy upto 1 μg.

Water diffusion Coefficient

The appropriate solution of the diffusion coefficient given by Crank [13] is

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2} \sum_{m=0}^{\infty} \frac{1}{(2m+1)^2} \exp.\{-D(2m+1)^2 \pi^2 t/l^2\} \qquad \textbf{Eqn. - 1}$$

if the uptake is considered to be a diffusion controlled by a constant diffusion coefficient D. Here M_t is the total amount of water absorbed by the film of thickness l at time t and M_∞ the equilibrium sorption attained theoretically after infinite time. The application of Eqn.-1 is based on the assumption that immediately the film is placed in the water, the concentration at each surface attains a value corresponding to the equilibrium uptake for the water existing and remains constant afterwards. The film is considered to be initially free of water. The value of t/l^2 for which the $M_t/M_\infty = ½$, conveniently written $(t/l^2)_{½}$ is given by

$$\left(\frac{t}{l^2}\right)_{1/2} = -\frac{1}{\pi^2 D} \ln\left\{\frac{\pi^2}{16} - \frac{1}{9}\left(\frac{\pi^2}{16}\right)^9\right\} \qquad \textbf{Eqn. - 2}$$

approximately, the error being about 0.001 percent. Thus we have

$$D = 0.049 / (t/l^2)_{1/2} \qquad \textbf{Eqn. - 3}$$

The water sorption isotherms are constructed by plotting M_t/M_∞ Vs. t/l^2 . The values of diffusion coefficient (D) were determined by using Eqn.-3, where $(t/l^2)_{½}$ is its value for which $M_t/M_\infty = ½$ in water sorption isotherms.

RESULTS AND DISCUSSION

The concept of preparing polyimide alloys via micromodification of polyamic acid with organic and inorganic micromodifiers, has been introduced [9-11] and the water uptake characteristics studies with Antimony pentachloride modifier have established that these alloys absorb water as low as 0.3 percent at the modifier concentration of 1.67×10^{-5} mol/L of polyimide. Such a low water uptake in polyimide alloys in comparison to unmodified one (2.7%) has evinced the interest in understanding the mechanism and as well as determining the extent of water uptake in other alloys prepared using this new concept. In the present study polyimide alloys are prepared by micromodification by a bifunctional epoxy modifier. The modifier concentration has been varied from 1.54×10^{-2} (i.e. critical crosslinker concentration or CCC) to as low as 1.54×10^{-6} mol/L. The water uptake experiment performed in the beginning have shown erratic results and it was attributed to the presence of residual solvent which leaches out into water used for the uptake experiments. This aspect has been previously observed [14] wherein the residual solvent has been removed by refluxing the polyimide films in methanol for a prolonged period. Accordingly, PI-EP alloys were kept in methanol and the solvent was removed. This experiment has provided two different results viz. i) the total alcohol uptake by the alloys and, ii) the amount of the residual solvent (DMAC) which was present before it's outdiffusion in methanol and these results are shown in Fig. 1 and Fig. 2 respectively. The

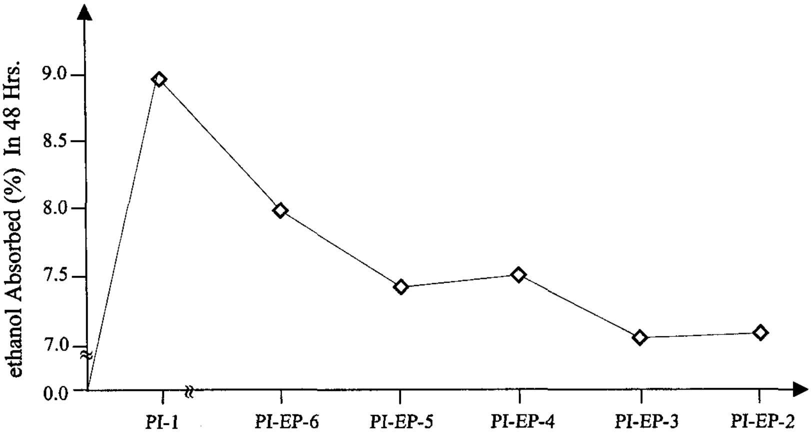

Fig. 1 : Methanol Absorbed (%) by PI & PI-EP Alloys.

methanol uptake was found to vary from 7.01 to 7.98 percent in PI-EP alloys whereas in the unmodified polyimide it was 9.0 percent. The alloy PI-EP-3 has lowest methanol uptake. The residual solvent content as expressed in percentage was found to vary from

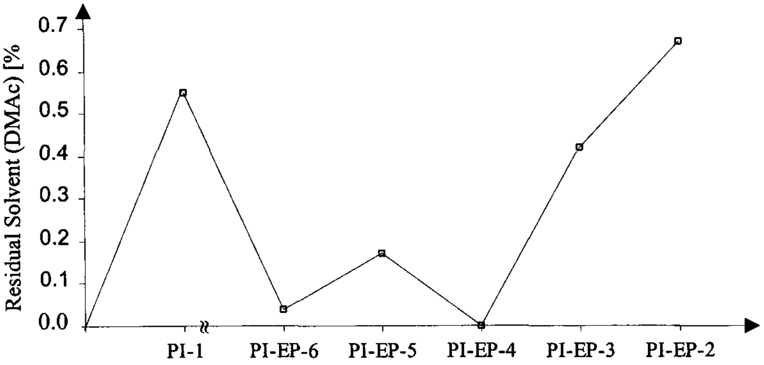

Fig. 2 : Residual DMAC Solvent in PI & PI-EP Alloys.

nil to 0.67 percent in PI-EP alloys and very interestingly a very negligible DMAC was present in PI-EP-4 (0%), PI-EP-5 (0.17%) and PI-EP-6 (0.04%). The presence of residual solvent in polyimide or its alloys can be visualized by the chemical reaction given in Fig. 3 wherein the starting polyamic acid has been shown as 4/1 complex of hydrogen bonded dimethyl acetamide with amic acid (structure I in Fig. 3). The 4/1 complexation has been reported previously [15]. The thermal imidization of this hydrogen bonded polyamic acid shall result in Polyimide macromolecules having fully imidized moieties (structure II-A) along with the residual partly uncyclized amic acid whose structure is shown in II-B in Fig. 3. It is therefore, possible to calculate the percentage of structure II B in complete macromolecular structure i.e. II by following equation (Eqn.- 4)

$$R = \frac{174\,S \times 100}{574 \times S + (100 - S)\,382} \qquad \textbf{Eqn. - 4}$$

Where,

R = percentage of residual solvent (DMAC).

S = is the percentage of partly uncyclized amic acid or pyromellitamic acid available as hydrogen bonded with DMAC (i.e. IIB in Fig. 3).

174 = twice of the molecular weight of DMAC.

574 = molecular weight of the structure II B.

382 = molecular weight of the pyromellitimide repeat unit (i.e. II-A in Fig. 3).

The value of S can be calculated the simplifying Eqn.-4 which takes the form of Eqn.-5.

$$S = \frac{38.2\,R}{17.4 - 0.192\,R} \qquad \textbf{Eqn. - 5}$$

The results of the calculated values of the percentage of structure II-B in the complete structure II for polyimide (neat) and its alloys with epoxy are presented in Table 1, which also includes the value of the residual solvent for better clarity. It is evident from Table 1 that PI-1 and PI-EP-2 contain maximum unimidized structure whereas the remaining PI-EP alloys possess much lower unimidized moieties. These values are indicative only as one needs to conduct the experiment more rigorously. Nevertheless, these experimental results have enabled to determine the residual solvent content which has not been hitherto reported elsewhere and as well as revealed the possible mechanism of the presence of this residual solvent in fully imidized polyamic acid. It is interesting to note that the

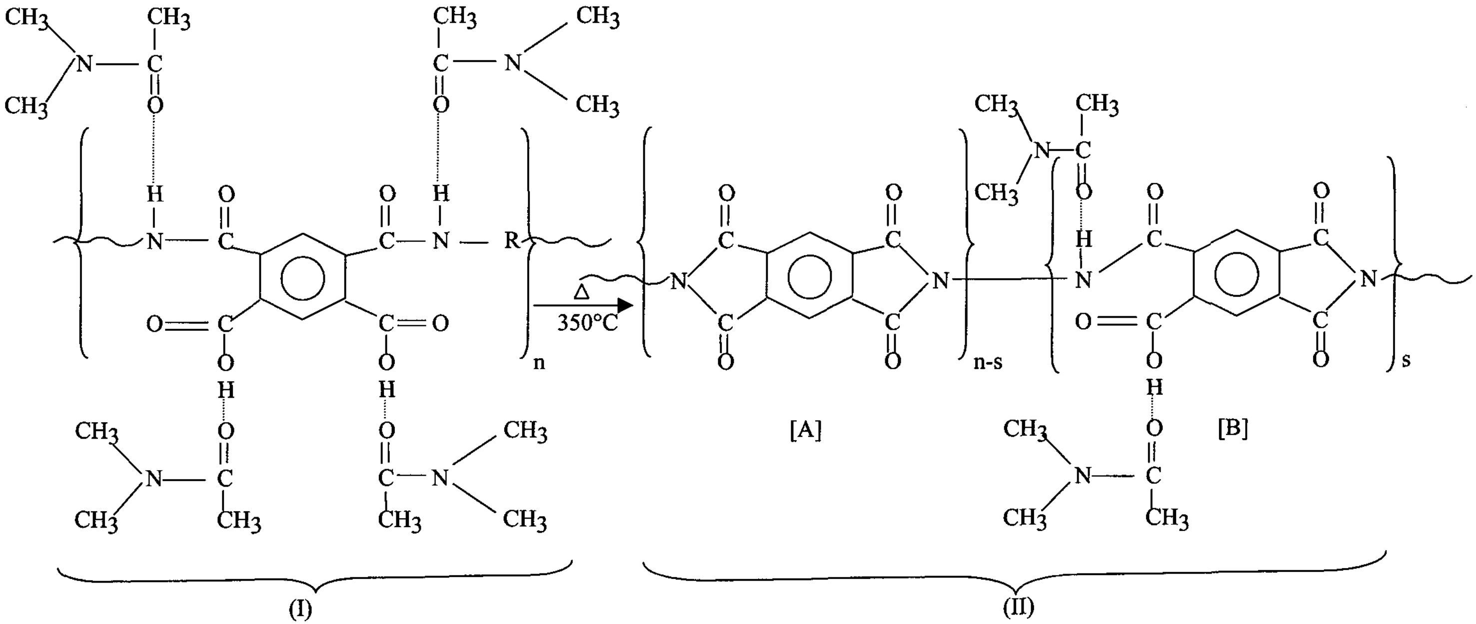

Fig. 3 : The Chemical Reaction Showing the Thermal Cyclization of Polyamic Acid to Polyimide & Resulting in Partly Imidized Structure Containing Residual Solvent.

commercial polyimide i.e. Kapton of 'Dupont' have also been reported to contain traces of residual solvent [16].

TABLE 1 : Percentage of the uncyclized polyamic acid moiety in structure II of Fig. 3 and percentage of the residual solvent (DMAC).

Sample Designation	Uncyclized PAA (%)	Residual Solvent (%)
PI-1	1.21	0.55
PI-EP-6	0.08	0.04
PI-EP-5	0.37	0.17
PI-EP-4	0.00	0.00
PI-EP-3	0.88	0.42
PI-EP-2	1.48	0.67

The water sorption in PI-EP alloys having the varied concentration of modifier and their neat version was measured as a function of time. The water sorption isotherms constructed from these experiments are shown in Fig. 4. The water absorption isotherms of all the

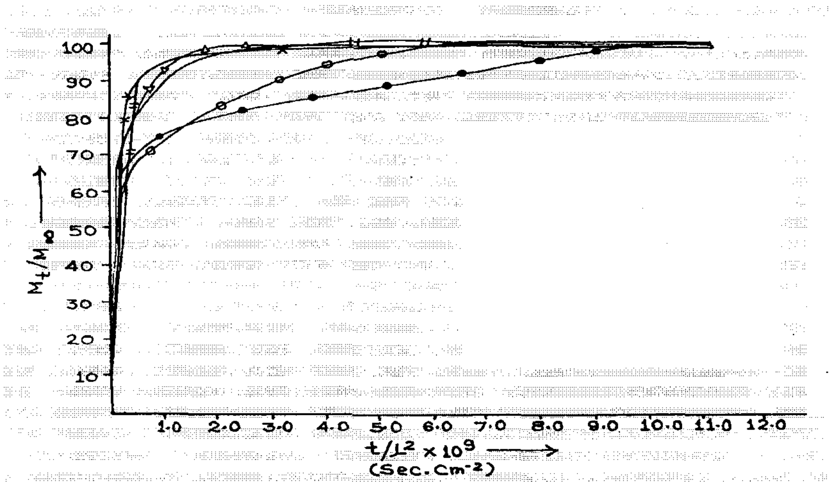

Fig. 4 : Water Sorption Isotherms of PI-EP Alloys & Neat PI

o—o = PI-1, △—△ = PI-EP-6, ×—× = PI-EP-5, ||—|| = PI-EP-4, —— = PI-EP-3, •—• = PI-EP-2.

PI-EP alloys were reasonably Fickian in nature, however, PI-1 and PI-EP-2 have shown a small departure from the Fickian behaviour. The values of the water sorption in 24 hrs (which could be considered as equivalent to the one determined as per ASTM D-570) and at equilibrium conditions are given in Table 2. The degree of imidization of PI-EP alloys which was determined by IR spectroscopic method and considering the neat PI as 100 percent, are also given in Table 2. It can be seen from the Table 2 that PI-EP-6 and PI-EP-5 have shown 20 to 25 percent less water uptake than its neat and this trend is followed in the equilibrium water sorption also. The maximum water sorption had occured in PI-EP-2 samples which contains the highest crosslinking density since PI-EP-2 has been imidized to 90.2 percent, its high water sorption could be attributed to uncyclized amic acid residues (~10%) as they have been found to be responsible [17] for higher level of water than their fully imidized version. The water sorption data are found to be consistent with the observation in respect of methanol sorption. These observations have estabilished that PI-EP alloys absorbs relatively lower water in comparison to neat and the alloy having the modifier concentration equal to CCC. The values of the diffusion coefficient have shown a little scatter but these values for PI-EP-5 and PI-EP-6 were respectively 3.3 and 2.5 times higher than PI-1 (i.e.neat). These higher values of diffusion coefficient for

TABLE 2. Water Sorption, diffusion coefficient and degree of imidization of PI-EP-alloys.

Physico-chemical Properties	Sample Designation					
	PI-1	PI-EP-6	PI-EP-5	PI-EP-4	PI-EP-3	PI-EP-2
Degree of Imidization (%)	100	98.8	96.7	95.0	92.1	90.2
Water sorption (%) at 24 Hrs.	2.99	2.31	2.21	2.47	2.58	3.25
Equilibrium Water Sorption (M_∞) (%)	3.14	2.39	2.24	2.50	2.60	3.30
Diffusion Co-efficient (D)x10^{-9} (cm^2sec^{-1})	0.49	1.22	1.63	0.22	0.37	0.44

PI-EP-5 and PI-EP-6, despite their absorbing very low water could be explained on the basis of the mechanism of the transport of the water molecules. It has been suggested by John *et al* [18] that the water molecules squeeze between the polyimide chains and if the large quantity of the water gets sorbed in the begining it may constrain local chain motions neccessary to permit penetrant molecules (water) to move through the glassy polymer. Due to the high values of the diffusion coefficient of PI-EP-5 and PI-EP-6, the large quantity of water may enter between the polymer chain in the begining itself. The initial higher water sorption will not allow more water to enter in chains and hence these alloys have shown lower water uptake. However many factors like the polymer crystallinity, free volume fraction and the imidization conditions should be considered to elucidate the mechanism of the water sorption and diffusion in these polyimide alloys. The detailed investigations in this regard are underway.

CONCLUSIONS

The PI-EP alloys prepared by recently developed concept involving in-situ generated blends by micromodification, have exhibited 20 to 25 percent lower water uptake than the unmodified PI. Despite the scatter in diffusion coefficient values, the mechanism of the water sorption and its transport within these alloys have been explained. The behaviour of methanol uptake is more or less similar to the water sorption.

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