Mechanical and electrical properties of polyimide blend films

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The preparation and characterization of two novel polyimide, one from pyromellitic dianhydride (PMDA)-4,4'-oxydianiline (ODA) and the other from 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA)-ODA, blend films with nylon 6 were reported earlier1,2. PMDA-ODA and nylon 6 blend films have shown up to 14.7% increase in Young's modulus and 25% increase in tensile strength at lower elongation over those of control films, whereas the same films have shown around 4.6% decrease in ultimate tensile strength (except the film PB2 which shows about 1% increase in ultimate tensile strength). BTDA-ODA and nylon 6 blend films have shown 19% higher ultimate tensile strength as well as 42% higher Young's modulus and 47% higher tensile strength at lower elongation. But in general the dielectric constant of the blend films (both BTDA and PMDA based) measured at 23°C, 100°C and 200°C and at 1.5 and 10 kHz frequency increases with increase in the percentage of nylon 6 in the blend and the breakdown voltage decreases with the increase in nylon 6 content in the blend films.

Polyimides are a class of high performance polymers having very good mechanical strength and electrical insulation characteristics, high thermal stability and chemical resistant properties3,4. Having these properties polyimides are used in aerospace and microelectronics industries5-7. Many new polyimides have been synthesized to overcome their processability problems. Also many blends of polyimides have been prepared8-12. But in these blends the reports on miscibility studies predominate rather than their property evaluation even in the miscible blends.

In earlier communications1,2 the preparation and characterization of cost effective blends from two different base polyimides with nylon 6 was reported. In this paper the mechanical and electrical properties of the same blend films are discussed.

Experimental Procedure

Materials

The materials, which were used for this study are as follows: 1,2,4,5-benzene tetracarboxylic dianhydride or commonly known as pyromellitic dianhydride (PMDA), 4,4'-oxydianiline (ODA) (Fluka, Switzerland), 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA) (Gulf Oil Corp. USA), ε-caprolactam, magnesium sulphate, calcium chloride, acetic anhydride, diphosphorus pentoxide, DMF. All the chemicals were of AR grade and they were purified by following standard methods13.

Method of preparation of film

At first two different poly(amic acids) (PAA) were synthesized from PMDA-ODA and BTDA-ODA in DMF following the standard procedure14. In this investigation four different compositions of blend films were prepared from each poly (amic acid). In each case of blend preparation a certain amount of the ε-caprolactam (depending on the solid PAA in the solution of PAA) and poly(amic acid) solution were weighed accurately in sequence in a weighing bottle. Then they were mixed thoroughly for about 30 min to get a homogeneous mixture. From that homogeneous mixture films were cast on clean glass plates. At first these sticky films were dried under vacuum and then

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thermally cyclo-dehydrated to get a blend film in each case and the complete scheme for this preparation has been shown in Scheme 1 and the blend formulation is presented in the Table 1.

Sample preparation for tensile property measurements

Tensile properties were evaluated according to ASTM D 882-91 using an Instron Tensile Tester 4302 (Universal Tensile Testing Machine) and average of 3 samples were taken. All the experiments were carried out at a jaw speed of 50 mm/min and film size was 10×100 mm. Thickness of the films (75-100 μm) were measured at 6-7 places and the average thickness [using a Mitutoyo (Japan) Thickness Gauge] was taken as the film thickness. After this all the films were conditioned in an air circulating oven for 48 h at 50±3°C. Before testing the film sample was taken out from oven and allowed to attain room temperature by keeping in a desiccator.

Sample preparation for dielectric constant and breakdown voltage measurement

In order to measure the capacitance of the films, they were coated with silver paint in a circular fashion in the following way: A cleaned rectangular aluminium foil of size about 8×4 cm was folded to make a square of about 4 cm square. The folding line was creased properly. A circular hole was made at the middle of the folded aluminium square by punching with a sharp cork borer. The film to be taken for testing was then sandwiched into the folded aluminium square to cover the circular hole of the folded square. The film in between the foils was clamped and then colloidal silver paste was coated on both the surfaces of the film exposed at the circular hole to ensure good contact with the condenser plates. The system was then dried under vacuum, the film was taken out from the folded aluminium square and the silver coated circular disc thus obtained on the film was used for electrical measurement.

The capacitance and dissipation factor of the film samples were measured using a GR-1620 AP capacitance measuring assembly at three frequencies of 1, 1.5 and 10 kHz at 23°C, at 100°C and at 200°C. From the capacitance (C) and dissipation factor values (D), the dielectric constant (ε) and loss factor (tan δ) have been calculated using following mathematical relations:

**Dielectric constant (ε)**

Self-capacitance \(C_0\) of the films was calculated from the relation:

\[ C_0 = \frac{A}{4\pi d} \]  \[ \text{(1)} \]

where \(A\) is the area of the silver coated circular film in square cm and \(d\), its thickness in cm. As the measurements were done on circular films in air, Eq. (1) becomes

\[ C_0 = 0.089 \times \text{area/thickness} \]  \[ \text{(2)} \]

in picofarad (pf). The dielectric constant (ε) of the film under examination was then calculated using the formula,

\[ \varepsilon = C/C_0 \]  \[ \text{(3)} \]

where \(C\) is the capacitance of the specimen film obtained directly from the measuring instrument.
loss factor, \( \tan \delta \), was calculated by multiplying dissipation factor \((D)\), obtained directly from the instrument, by the respective frequency \((f)\) in kHz i.e.,
\[
\tan \delta = D \times f 
\]

**Volume Resistivity \((R)\)**—As the volume resistivity of most of the polyimides is very high, their ac volume resistivity value was calculated using the formula\(^6\)

\[
\log R = 19 - 2(\varepsilon - 2) 
\]

where \( R \) is volume resistivity and \( \varepsilon \) is dielectric constant.

**Breakdown Voltage**—Breakdown voltage of all the test films was measured using a Siemens Instrument at 53-55 Hz and increase of voltage during measurement was 500 v/s up to the breakdown voltage as per ASTM D-149-94. Breakdown voltage was directly obtained from the instrument. Average of two specimen data was taken. Flat circular films were placed in air between 4 mm diameter brass electrodes with 2 cm edge radius for the experiment and maximum ambient relative humidity was 89%.

### Results and Discussion

**Tensile property measurement**

Figures 1 and 2 show the stress strain behaviour of the PMDA and BTDA based blend films. From Fig. 1 it is observed that the PMDA based blend films show slight decrease in tensile strength but an increase in elongation at break. But in case of BTDA based blend films tensile strength increases compared to the control film but a decrease in elongation at break is observed.

From Figs 1 and 2 it is found that the tensile strength of the BTDA based films is higher compared to that of PMDA based films, but the elongation at break (EB) which is a very much desired property of this type of polyimide films is sufficiently lower for BTDA based films compared to PMDA based films. In the two systems studied the chemical structures of the dianhydrides are different (Scheme 1). The benzophenone carbonyl in BTDA exerts additional intermolecular interactions, which determines the low elongation at break. This very strong intermolecular interaction in BTDA based system studied prevents polymer chain slippage and as a result elongation is lower. This strong intermolecular interaction originates from the interaction between the electron rich ‘O’ of ODA moiety and electron deficient benzophenone carbonyl moiety in BTDA.\(^7\) This strong interaction is also reflected in other properties, mainly high chemical stability of BTDA based film.\(^8\) But in PMDA based film the above mentioned interaction is absent and as a result molecular chain slippage during tensile testing provides higher elongation at break (~250-500 % higher) compared to BTDA based films. The blend films of PMDA based system show some decrease in tensile strength property but the elongation at break are higher or equivalent to that of the control film. This decrease in tensile strength may be due to the presence of nylon 6
The stress versus strain curves are steeper for all the blend films (except BB 3 and BB 4) and overall the slopes are higher in BTDA based films compared to the PMDA based films. This may be due to various reasons like favoured orientation or crystallization during preparation of films or the higher interchain attractions.

Young's moduli for all the blend films (except BB 3 and BB 4) at low strain (0.01-0.04) are higher compared to the respective control films. The Young's modulus is shown in Fig. 3 for PMDA and BTDA based systems.

Again the modulus of the PMDA films at 20% elongation and modulus of BTDA films at 6% elongation shows (Fig. 4) that all the blend films have got higher modulus. The toughness of all the films were calculated from the area under the stress-strain curve and are presented in Table 2.

It is observed from Table 2 that the toughness of the PMDA based blend films is higher as compared to that of the control film, whereas the reverse trend is observed in case of the BTDA based blend films. It is well known that nylon 6 is a tough material, so when the amount of nylon 6 in the PMDA based blend films increases toughness increases but why the BTDA based blend films behave in the opposite manner is not very clear. It may be due to the completely different type of interaction of nylon 6 with the base polyimide.

Dielectric constant, dissipation factor and volume resistivity

The dielectric constants of all the PMDA and BTDA based blends and control films and their variations with temperature and frequency are presented in Figs 5 and 6 respectively.

It is observed that the dielectric constants decrease with increase in the frequency from 1 to 10 kHz. This may be explained in the following manner: at low frequencies the alternating accumulation of charges at the interfaces between different phases of the polymer system takes place but at higher frequencies the accumulation of charges is caused by the polarization with dipole orientation.

The Fig. 5 shows an overall decreasing trend of $\varepsilon$ with increase in frequency as well as temperature.
However this trend in $\varepsilon$ variation is not followed in PB 2 and PB 4 films at 100°C for some unknown reasons. The BTDA based blend films also behave in a similar fashion as observed for the PMDA based blend except for the film BB 1, which shows lower dielectric constant values compared to the control film (BB 0). The reason behind this type of behaviour is not clear.

Also the higher dielectric constant values of the blend films may be due to the lower free volume in these blends as evidenced from higher density also attributed higher dielectric constant values to the lower free volume. The dissipation factors vary from 0.0003 to 0.0230 depending on the composition of the films, temperature and frequency.

Volume Resistivity of all the films at various temperature and frequencies were calculated from Eq. (5) and it was in the order of $10^{16}$.

**Breakdown voltage or dielectric strength**

The breakdown voltage for all the films is presented in Table 3.

From Table 3 it is observed that for the PMDA based blends the value of breakdown voltage decreases with the decrease in the percentage of base polyimide. This is due to the fact that when the percentage of polyimide decreases and substituted by nylon 6 the energy required for bond rupture and generation of ionic species becomes easier at lower voltages in an aliphatic system like nylon 6. Ultimately these ionic species becomes the carrier of current and rupture of film takes place at a lower voltage. For the BTDA based films also the aforementioned reason is applicable except the film BB 3.

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**References**