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A novel cross-linked polyimide film: synthesis and dielectric properties

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Abstract

A novel cross-linked polyimide (CPI) has been prepared by imidization of cross-linked poly(amic acid) (CPAA). In this work, the Ac conductivity and dielectric properties of this polyimide are presented comparitively with those of conventional polyimide (PI), in the 0.2–100 kHz frequency range and 300–463 K temperature interval. Although the frequency and temperature dependencies of dielectric constant of both conventional and cross-linked polyimides show the same behaviour, the dielectric constant of CPI takes lower values. The Ac conduction studies suggest that electron hopping is responsible for conduction of the PI and CPI films. The activation energy calculated in 296–353 K temperature interval and the ß-relaxation was also observed for CPI.

Keywords: Polyimide; Dielectric constant; AC conductivity

1. Introduction

Polyimides have many desirable characteristics such as excellent mechanical properties, low dielectric constant, low relative permittivity, high breakdown voltage, inertness to solvent and radiation resistance. They are distinguished from other high performance polymers by the solubility of poly(amic acid) precursor form, which can be casted into uniform films and quantitatively conversion to polyimide. Polyimides have been especially used widely in microelectronic, film, adhesive and membrane industry [1–7] due to these prior properties.

One of the most important applications of polyimide thin films is used as the inter level dielectric insulators within LSI. The polyimide films that are most widely used in the microelectronic industry with low relative permittivity (dielectric constant) have values in the range of 2.9–3.4 [7]. The utmost importance for the microelectronic applications is the lowness of dielectric constant and high dielectric breakdown voltage of polyimides. In electronic packing, low dielectric materials minimize cross talk and maximize signal propagation speed in devices. Hence, the development of polyimides with increasingly lower dielectric constants has been the focus of several investigations [7–13]. In particular, fluorinated polyimides have received extensive attention due to their lower dielectric constants suitable for the microelectronic applications. Simpson and St Clair [14] well described the routes for lowering dielectric constants. Among the strategies used to lower dielectric constants in polyimides are as follow: incorporating diamine and dianhydride reactants which minimize polarizability, incorporating diamine and dianhydride reactants which impart a high degree of free volume and incorporating fluorine atoms into the molecular structure of the polyimide.

Hougham et al. [7,8] and Onah et al. [9] mainly interested in fluorine introduction to polyimide structure in order to decrease dielectric constant. They reported that the incorporation of fluorine into polyimide structure has been intensively explored in the past decade and also fluorine amount increasing has been found to generally lower the dielectric constant and moisture absorption. On the other hand Cassidy et al. has reported the effect of fluorination on polyamide whose dielectric constant nearly in the range of 2.6–3.0 [10].

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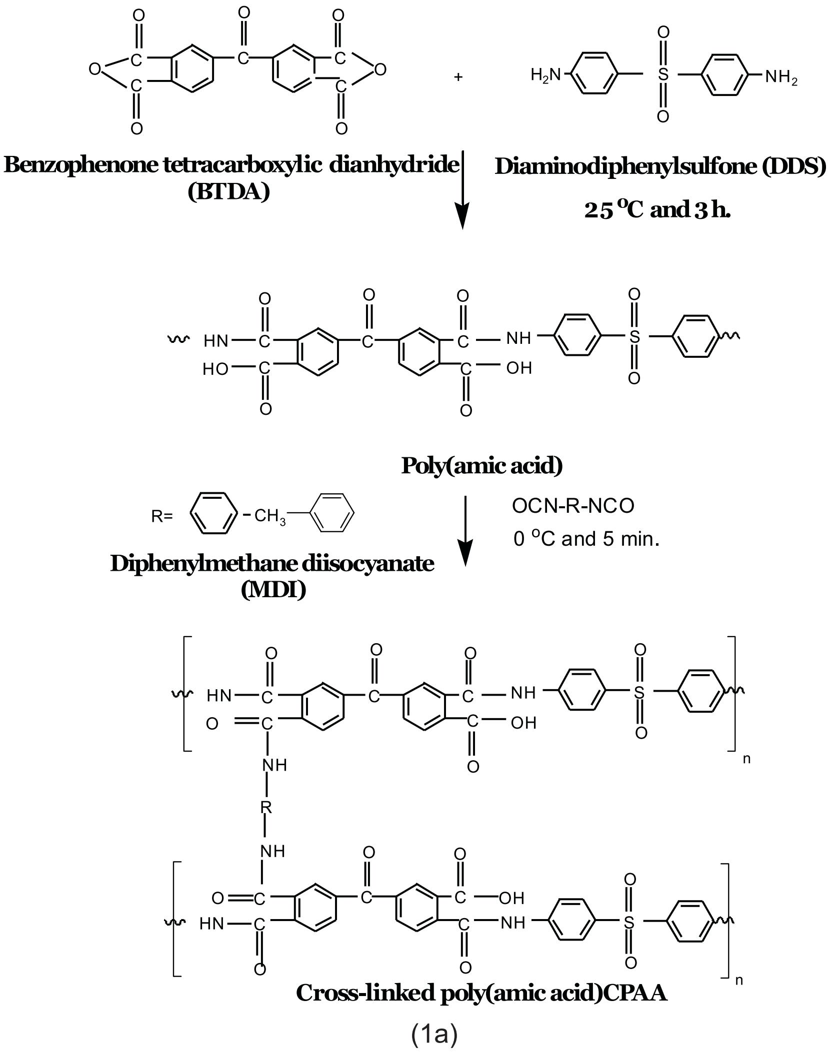


Fig. 1. (a) Chemical structure of PAA and CPAA. (b) Chemical structure of CPI.

According to Yamazuki et al., the cross-linking in the PI structure may form a porous structure and this may give the films with a low dielectric constant [15]. To best of our knowledge no study has been reported on the dielectric properties and relaxation process for a cross-linked polyimide films so far. But, there is only limited relaxation studies on conventional polyimides [16–18].

In this work, our main aim was to prepare and check the dielectrical properties of a cross-linked PI film with lower dielectric constant. We present the FT-IR characteristic, the thermal and dielectric properties and also the Ac conduction of a novel cross-linked polyimide prepared by imidization of cross-linked polyamic acid (CPAA) obtained by the reaction of conventional poly(amic acid) (PAA) and diphenyl methane diisocyanate. We also prepared and present the electrical properties of an anolog conventional PI for comparison. Furthermore, the ß-relaxation and activation energy for CPI are investigated for the first time. We expect that we could get some preliminary information of relaxation process of cross-linked polyimide thin films.

2. Experimental

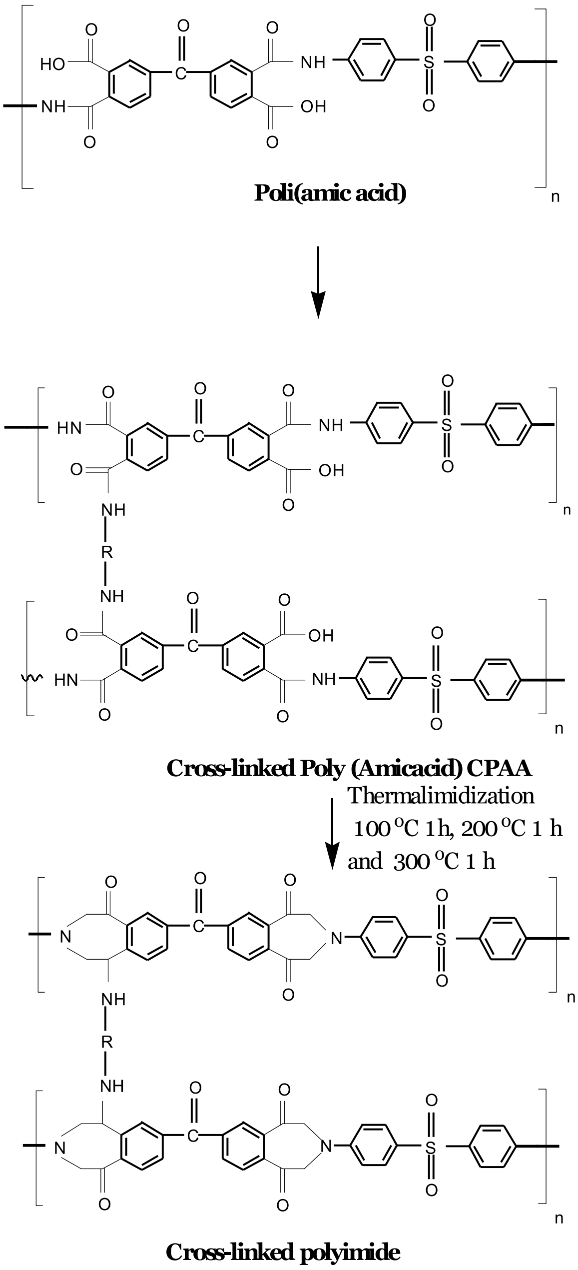
2.1. Materials

Benzophenone tetracarboxylic dianhidryde (BTDA, purity > 97), diaminodiphenyl sulphone (DDS, purity > 99) and diphenyl methane diisocyanate (MDI, purity > 97) were received from Merck Company, Germany and they were used without any further purification. *N*-Methyl pyrolidone (NMP) was distilled over CaH_2 and dried over a molecular sieve, 5 Å.

2.2. Synthesis

2.2.1. Preparation of conventional poly(amic acid) (PAA)

The diamine compound dissolved in dry NMP was placed into a 100 ml three-necked round bottomed flask equipped with a thermometer, magnetic stirrer, oil bath and nitrogen inlet–outlet system. An equivalent of dianhydride BTDA (6 mmol) was slowly added into



(1b)

Fig. 1 (*continued*)

well stirred DDS (6 mmol) solution in NMP solution (solid 10% (w/v)) at 30 °C for 3 h under N_2 atmosphere. After this time, reaction was stopped and the reaction solution was kept in a freezer to prevent any further proceeding of the reaction.

2.2.2. *Preparation of cross-linked poly(amic acid) (CPAA)*

CPAA was prepared by the reaction of PAA (6 mmol) and equivalent amount of MDI as a cross-linker to the carboxylic acid groups of PAA, at 0 °C for 5 min under N_2 atmosphere. MDI dissolved in NMP was added with a dropping funnel into PAA solution in 5 min. The mixture was strongly stirred for further 5 min, subsequently reaction was stopped and immediately the film was prepared by doctor blade technique with a 50 μm knife on a well cleaned glass substrates. We preferred to use this technique in order to avoid the coating difficulties, such as existence of pinholes which cause short circuit between electrodes [19], a need of special apparatus to coat film on an electrode (spin coating and chemical vapour deposition [20]) and measurement of the coated film thickness. In Figs. 1(a) and 1(b) the chemical structure of both PAA, CPAA and CPI are shown.

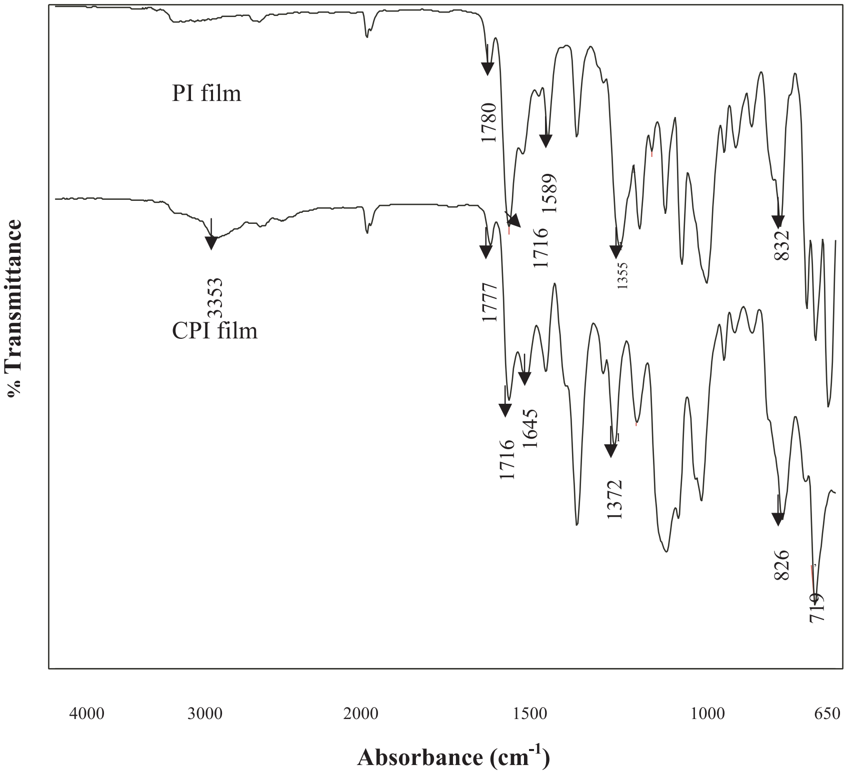


Fig. 2. FT-IR spectra of conventional and cross-linked polyimide film.

2.2.3. *Preparation of conventional polyimide (PI) and cross-linked polyimide (CPI) films*

Conventional and cross-linked modified polyimide (PI and CPI) films have been prepared by thermal imidization at 100 °C for 1 h, 200 °C for 1 h, 300 °C for 1 h under N_2 atmosphere in a temperature controlled oven. After the thermal treatment, the films have been removed from the glass plate by immersing into hot water. Subsequently the self-standing films were obtained and dried in a vacuum oven.

3. Measurements

FT-IR analyses of PI and CPI films were carried out by Perkin Elmer spectrum one with the ATR (attenuated total reflection) technique. Thermal and oxidative degradations were performed using a Linseis L31 TGA/DTA system. The samples were heated from room temperature to 750 °C under air atmosphere at the heating rate of 5 °C/min. Moisture uptake values were calculated from the weight changes of the films between drying at 80 °C for 10 h in a vacuum oven and keeping in a box with 55% relative humidity. They were kept in a box with 55% relative humidity (RH) for 1 week. The solubility tests were carried out by immersing the films into various solvents for one week at both room temperature and hot (60 °C).

The base and counter Au electrodes, each of 3000 Å thick, were evaporated and deposited onto the polyimide films in a 10^{-5} Torr vacuum. In this way, Au/polyimide film/Au sandwiches were ready for the measurement of dielectric properties of the PI and CPI films. Electrical contacts were made by indium on Au electrodes with copper wires. The thickness of the self-standing films were measured by means of a stylus profilometer and found to be 6 and 7 μ for PI and CPI films, respectively. A travelling microscope was used for the determination of the capacitor areas ($\sim$10 mm^2). Dielectric strength of the films were measured with Electrotechnic Laboratorium D-7015 'Insulation Breakdown Tester' UH270, with resolution of 50 V for 2.5 kV and 100 V for 5 kV.

For capacitance and dissipation factor measurements a Gen-Rad 1615-A Scheering Bridge, a Gen-Rad 1232 Null Detector and a Sony-Tektronix AFG100 Generator were used. Temperature measurements were carried out with a digital platinum thermocouple (PT100) control unit. The Ac measurements were made in an approximately 10^{-3} Torr vacuum.

4. Results and discussion

Physical and chemical properties of PI and CPI films are presented in Fig. 2. The same experimental results were obtained under the same conditions.

4.1. *FT-IR spectra of the films*

Structures of the films were characterized by FT-IR with ATR (attenuated total reflection) and the spectrum of both films are shown comparatively in Fig. 2. From the FT-IR results, we observed that expected imide bands have been determined after thermal imidization of the films. FT-IR spectra of PI showed characteristic imide bands at 1780 and 1716 cm^{-1} (C–O stretching), 1355 cm^{-1} (C–N stretching), 832 and 716 cm^{-1} (C–O asymmetric stretching). When the cross-linker is added, an absorption at roughly 2250 cm^{-1} corresponding to the isocyanate group is observed. This peak has disappeared after gelation and thermal imidization of polyimide thin films. FT-IR spectra of the CPI has the characteristic imide bands at 1777 and 1716 cm^{-1}(C–O symmetric stretching), 1372 cm^{-1} (C–N stretching), 826 and 719 cm^{-1} (C–O asymmetric stretching). It was also observed that the new absorption peaks at 3353 cm^{-1} (N–H stretching of primer and secondary amid) and the intensity of the peak in which 1645 cm^{-1} (C=O amide I) increased due to the formation of poly(amide–imide) structure during the preparation of CPI.

4.2. Thermal properties of the films

TGA curves of PI and CPI films are shown in Fig. 3. At a heating rate of 5 °C/min of TGA, it was observed that thermal and oxidative degradation of these films took place in one stage. Degradations are appeared in the range of 350–450 °C (10% weight loss) because of the degradation of imide backbone. CPI has lower thermal and oxidative degradation resistance than the conventional polyimide film due to the presence of amide groups in the structure.

4.3. Solubility, dielectrical breakdown strength and moisture uptakes

Solubility, dielectrical breakdown strength and moisture uptake properties of the PI and CPI films were performed and also discussed. *N*-Methyl pyrolidone (NMP), tetrahydrofurane (THF), dichloromethane ($MeCl_2$) and toluene were used as solvents for solubility experiments. Both PI and CPI films have shown the excellent solvent resistance in the chosen solvents at room temperature and hot (60 °C). On the other hand, dielectrical breakdown strength of CPI stays lower than that of PI. This is probably due to the higher amount of free volume in CPI film. PI and CPI have dielectrical breakdown strength 152.9 and 80.4 kV/mm, respectively. However, the value of dielectric breakdown strength of CPI is quite appropriate for many microelectronics applications. In addition, CPI was observed to have lower moisture uptake compared to PI. PI and CPI have moisture uptake values 1.71 and 1.18%, respectively. The materials to be used in microelectronic industry are highly preferred with high dielectrical breakdown strength and low moisture uptake.

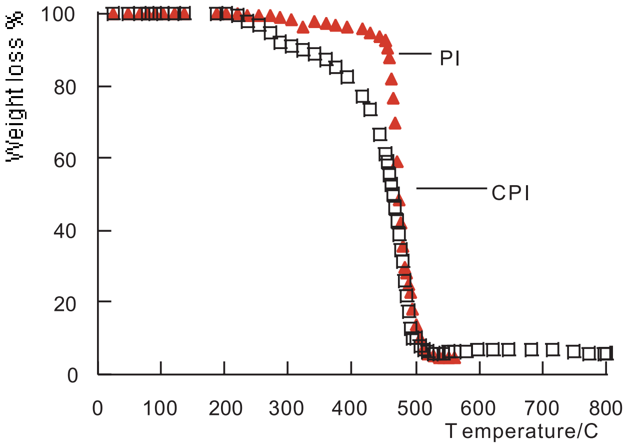


Fig. 3. TGA curves of conventional and cross-linked polyimide film.

4.4. Dielectric properties of the films

The frequency and temperature dependencies of dielectric constant, dielectric loss and Ac conductivity are investigated for both PI and CPI films. The characterization of temperature and frequency dependence of the dielectric constant is a very important factor to be considered dielectric materials for microelectronic applications of dielectric materials. In this study, a cross-linked polyimide film has been prepared. Cross-linking caused a network structure formation. This structure effectively restricts orientation and relaxation of dipoles and thus decrease the dielectric constant and dissipation factor.

4.4.1. Frequency and temperature dependence of Ac conductivity

The Ac conductivity of both polyimide films has been calculated from the measured values of the capacitance, dissipation factor and capacitor area for each frequency at various temperatures. Using the obtained data, the frequency dependence curves of Ac conductivity for PI and CPI films, at various temperature values between 294 and 463 K, are drowned in Figs. 4 and 5, respectively.

On the other hand, it is well known that the frequency dependence of Ac conductivity, $\sigma_{\mathrm{Ac}}(\omega)$, can be fitted by

$$\sigma_{\mathrm{Ac}}(\omega) = A\omega^{s} \tag{1}$$

for several low mobility polymers and even for crystalline materials. Here, ω is the angular frequency, s is the frequency exponent and A is a temperature independent constant [21–23]. By fitting our data to Eq. (1) we found s values. Values of frequency exponent (s) for both the PI film and the CPI film decrease with increasing temperature as shown in Figs. 4 and 5, respectively. It is consistent with the results reported for amorphous materials [3,22].

4.4.2. Frequency and temperature dependence of dielectric constant

The dielectric constant ε_1 was calculated according to the usual parallel plate capacitor formula. The dielectric

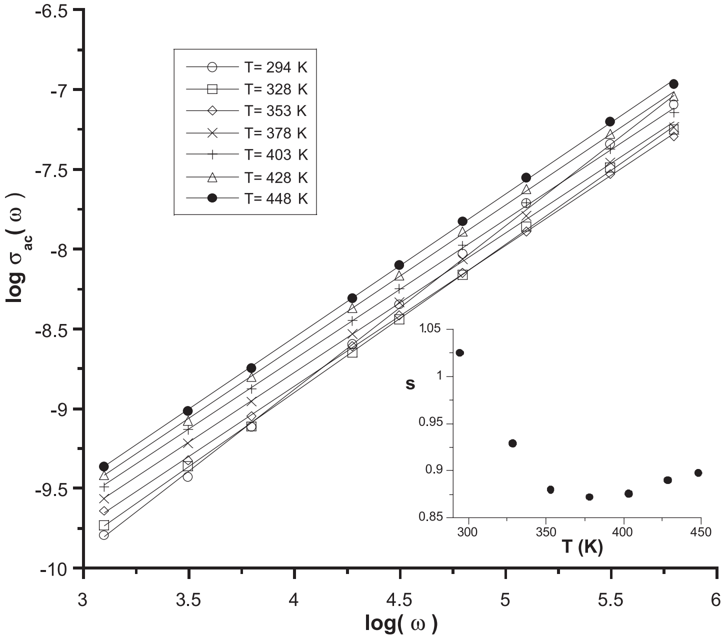


Fig. 4. Log Ac conductivity, $\sigma_{Ac}(\omega)$, vs. log ω and temperature dependence of s for conventional polyimide film.

constant dependence on frequency for both polyimide films at various temperatures is shown in Figs. 6 and 7. It is seen from these figures that ε_1 decreases with increasing frequency when temperature is kept constant. Furthermore, these curves keep their shapes but slide up at higher temperatures. These are in good agreements for thermoset and cross-linked polymers [24]. Dielectric constant of PI's, in general, are known to decrease gradually with increasing frequency [25]. This behaviour can be attributed to the frequency dependence of the polarization mechanisms. The dielectric constant depends upon the ability of the polarizable units in a polymer to orient fast enough to keep up with the oscillations of an alternating electric field. When frequency increases the orientational polarization decreases since the orientation of dipole moments need a longer time than electronic and ionic polarizations. This causes the dielectric constant ε_1 to decrease. The increase of ε_1 towards the low frequency region is also seen from Figs. 6 and 7. This may be attributed to the blocking of charge carriers at the electrodes [3]. On application of the field, charges in the dielectric films migrate because of the impedance to their motion at the electrodes and space charge and macroscopic distortions result.

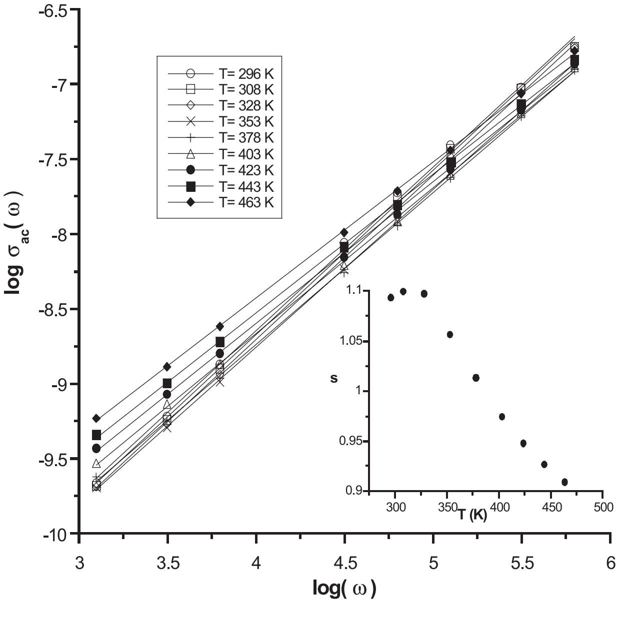


Fig. 5. Log Ac conductivity, $\sigma_{Ac}(\omega)$, vs. log ω and temperature dependence of s for cross-linked polyimide film.

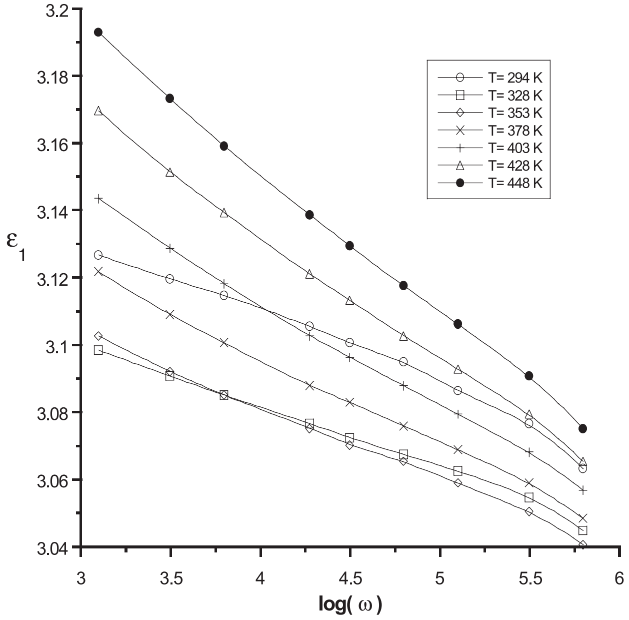


Fig. 6. Dielectric constant ε_1 vs. frequency for conventional polyimide film.

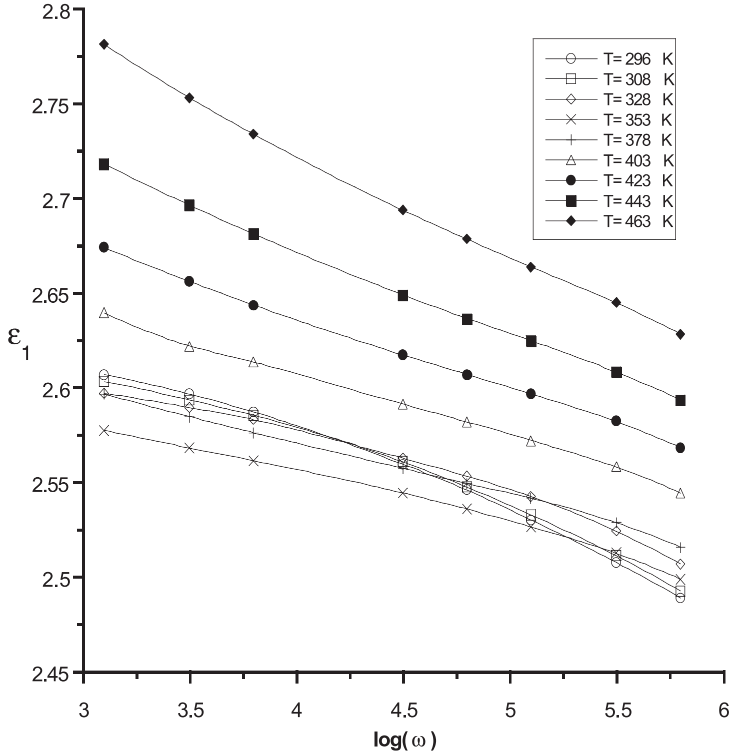


Fig. 7. Dielectric constant ε_1 vs. frequency for cross-linked polyimide film.

CPI has slightly lower dielectric constant than the other anologs reported by Hougham et al. and Simpson et al. They reported that the dielectric constants are in the range of 2.6–2.9 for the symmetrical and unsymmetrical fluorine substituted PI films.

Fig. 8 shows the variation of the dielectric constant ε_1 with temperature at various frequencies for both polyimide films. It is clear that ε_1 increases with increasing temperature. For polar polymers the dielectric constant

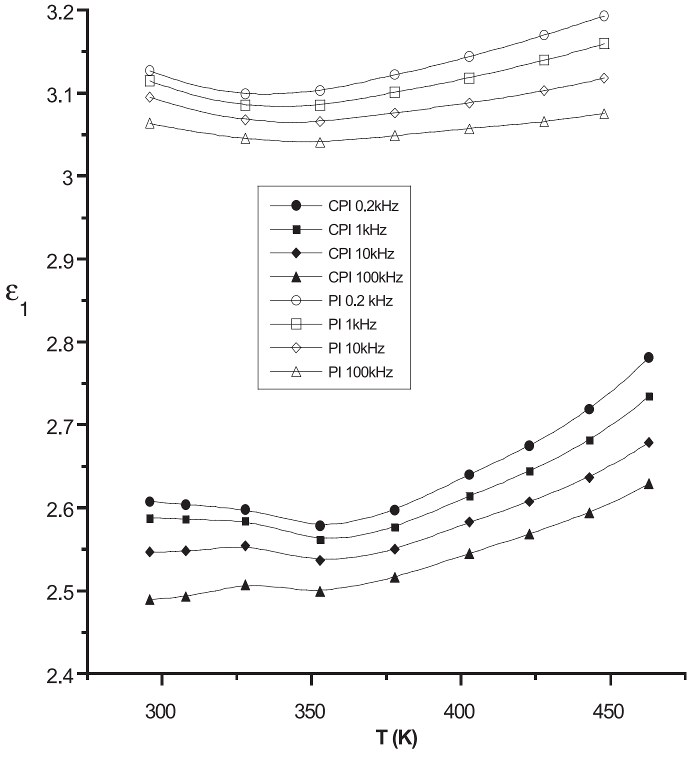


Fig. 8. Dielectric constant ε_1 vs. temperature for conventional and cross-linked polyimide film.

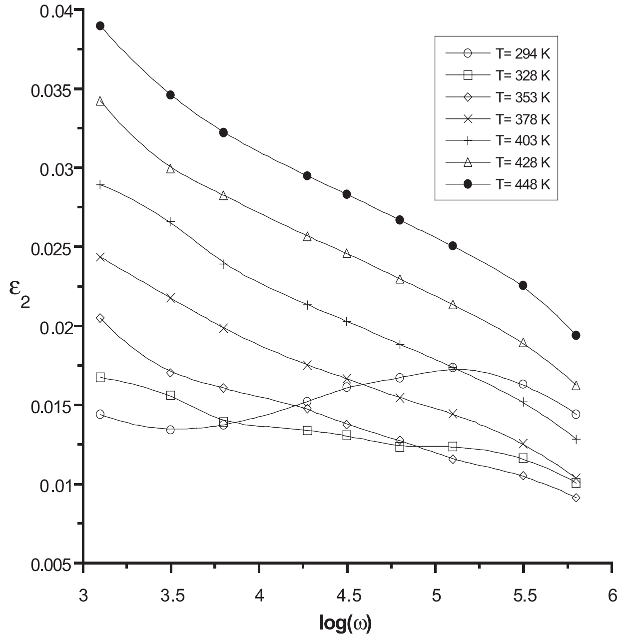


Fig. 9. Dielectric loss ε_2 vs. frequency for conventional polyimide film.

increases with increasing temperature [18]. For CPI, in the low temperature range, polar groups of polymers are difficult to orient and relax in the applied electrical field because of the molecular chain segments in glassy state. With increasing temperature, the chain segment mobility increases and polar groups start to move in response to the applied electrical field, which increase the orientation of polymer and dielectric constant. As seen from Fig. 8, the dielectric constant has exhibited small changes with temperatures. For many microelectronic applications, dielectric materials with stable dielectric constant and dissipation factor values across large frequency and temperature range are highly preferred.

Despite PI and CPI films have the same frequency and temperature dependencies, the dielectric constant of the CPI has lower values. This result confirms the restriction of orientation and relaxation of polar groups by the formation of network stability.

Another factor affecting the dielectric behaviour of a material is its chemical structure which influences charge distribution and thermal motion of dipoles.

4.4.3. Frequency and temperature dependence of dielectric loss

Figs. 9 and 10 shows the frequency dependence of dielectric loss ε_2 at different temperatures for PI and CPI films. It was observed that ε_2 increases as the frequency increases and reaches a maximum and thereafter decreases at 296–378 K temperature interval for CPI film. As the temperature increases the frequency at which ε_2 reaches a

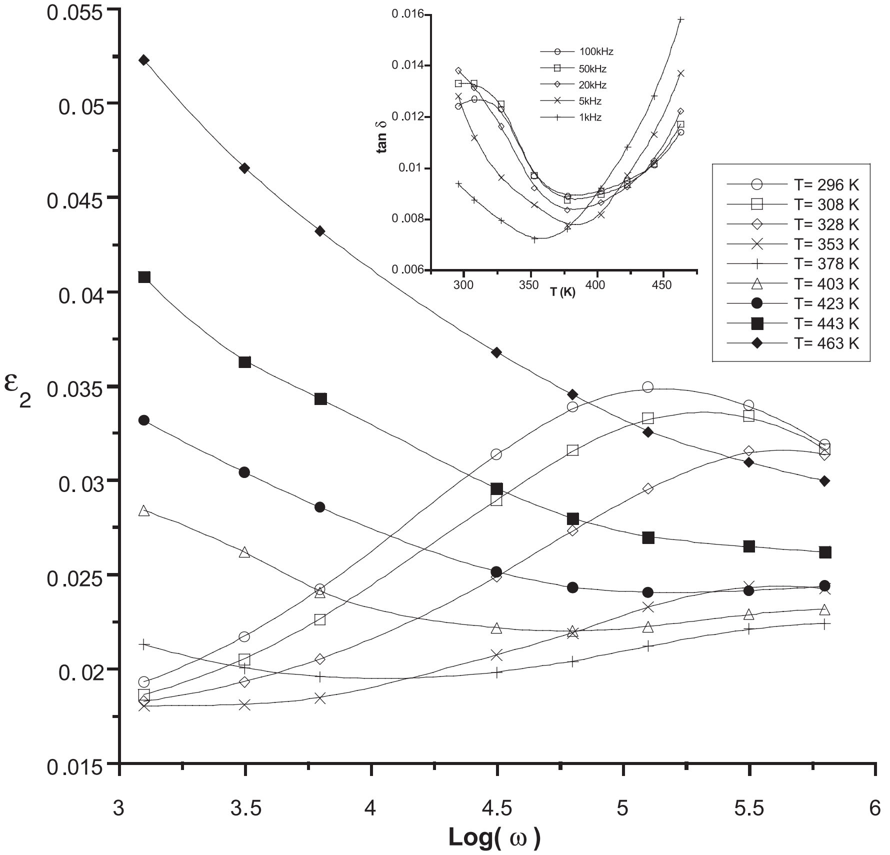


Fig. 10. Dielectric loss ε_2 vs. frequency and tan δ vs. temperature for cross-linked polymide film.

maximum shifted towards higher frequencies. The activation energy for the observed relaxation process was evaluated from the following equation

$$\omega_{\max} = \omega_0 \exp\left(\frac{\Delta E}{kT}\right)$$

where $\omega_{\max}$ is the frequency at which tan δ is maximum and ΔE is the activation energy. The plot of log $\omega_{\max}$ vs. $1/T$ is shown in Fig. 11. From the slope of the straight line one evaluates activation energy which was found to be 0.19 eV. The value of activation energy less than 1 eV indicates the predominance of electronic conduction in the present case. Thus it is concluded that Ac conduction in for CPI polymide films is due to electronic hopping. Many researchers have observed similar results in other insulating polymers [3,26].

4.4.4. Relaxation process

As is well known, aromatic polyimide and co-polyimide films exhibit several relaxation processes (α, β, γ) in their dynamical and dielectric behaviours [18]. In 300–463 K temperature range, we have interested in β-relaxation. This type of relaxation is called as subglass secondary relaxation. It is associated with phenyl ring motions and also is influenced by moisture absorption content, aging history and morphology. With increasing temperature, β-relaxation process is observed in the range of 50–250 °C during the thermal treatment of polyimides. An α-relaxation process attributed to glass transition can be normally observed at high temperatures (>300 °C).

As shown in Fig. 10, β-relaxation was clearly observed at 100 and 50 KHz as approximately 40 and 24 °C, respectively, for CPI. For PI, β-relaxation temperatures has not been observed in the same temperature range. β-Relaxation is related with rotation of rigid segments of phenylene or imide groups around flexible hinges such as SO_2 [18]. On the other hand, dianhydrides can also affect β-relaxation decreased with incorporation of flexible linkages in the dianhyrides. With increasing frequency, β-relaxation shifts toward higher temperatures in accordance with Arnhenius law. This result also is in good agreement with Ref. [18]. Sensitivity of β-relaxation to frequency is due to its lower activation energy.

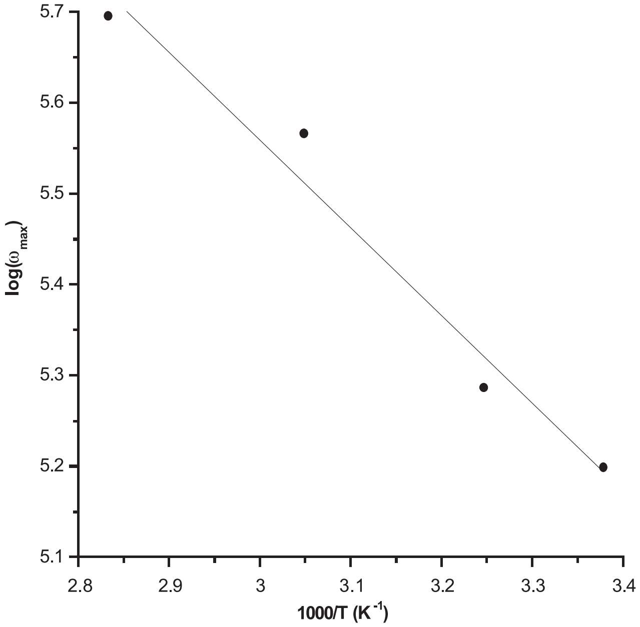


Fig. 11. Plot of log $\omega_{\max}$ vs. inverse absolute temperature of cross-linked polyimide film.

5. Conclusion

In this study, a novel cross-linked polyimide film (CPI) and conventional polyimide (PI) have been prepared by thermal imidization of cross-linked poly(amic acid) and conventional poly(amic acid). The dielectric constant and dielectric loss of the conventional and novel cross-linked polyimide films were found to be frequency and temperature dependent. It was found that this type of cross-linked polyimide is very promising for electrical applications due to its good thermal stability, excellent solvent resistance, low dielectric constant, low moisture absorption and stability in a various regions of frequencies. For CPI the activation energy was calculated for 300–350 K temperature interval and β-relaxation was observed above room temperature.

We conclude by saying that dielectric constant of the novel cross-linked polyimide film has lower values compared to dielectric constant of conventional polyimide film. So this type of novel polyimide films can be used as alternative dielectric layers in the microelectronic industry.

In the future studies, dc conductivity properties and detailed relaxation processes (including α, β and γ) will be studied in a wide temperature range for cross-linked polyimide films. β-Relaxation was clearly observed at 100 and 50 KHz as nearly 40 and 24 °C, respectively, for CPI.

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