

Thermal and Electrical Properties of some Poly(ether-imide) Thin Films

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Thin films, in the range of tens of micrometers thickness, have been prepared by casting onto glass plates the N-methyl-2-pyrrolidone solutions of two poly(ether imide)s containing isopropylidene or hexafluoroisopropylidene groups. The polymers have been synthesized by solution polycondensation reaction of 4,4'-(1,3-phenylenedioxy)dianiline, with 2,2-bis[(3,4-dicarboxyphenoxy)phenyl]propane dianhydride or 1,1,1,3,3,3-hexafluoro-2,2-bis[(3,4-dicarboxyphenoxy)phenyl]propane dianhydride. The dynamic mechanical analysis and dielectric spectroscopy were employed to study thermal and electrical behaviour of polymer films.

Keywords: poly(ether-imide)s, thin films, dynamic mechanical analysis, dielectric spectroscopy

High performance polymer films and coating materials are increasingly being required by the electronics industry for use as interlayer dielectrics and passivation coatings in integrated circuit fabrication. Dielectric materials used for thin film multichip modules must meet a number of requirements including a low dielectric constant, low dissipation factor, minimal moisture absorption, and high thermal stability [1, 2].

Aromatic polyimides are a class of polymers known for their high thermal stability, excellent electrical and mechanical properties, and good chemical resistance. Some of these polymers have been widely used in industry as structural materials or as insulating layers in integrated circuits [3-5].

It has been generally recognized that aromatic ether linkages inserted in aromatic main chain polymers lead to lower glass transition and crystalline melting temperatures as well as significant improvement in solubility and other processing characteristics of the polymers without greatly sacrificing other advantageous properties [6]. Poly(ether imide)s have received much attention because they can provide a compromise between good thermal stability and processability when compared to aromatic polyimides. These polymers were developed as a result of the requirement for high-performance materials that could be readily fabricated by standard plastic extrusion and injection molding processes [7-11].

The incorporation of hexafluoroisopropylidene (6F) groups into polymer backbone enhances the polymer solubility without sacrificing thermal stability. The 6F groups increase the glass transition temperature and flame resistance with a concomitant decreased of crystallinity and water absorption. The bulky 6F groups also serve to

increase the free volume of the polymers, thus improving its electrical insulating characteristics [12- 17].

Dynamic mechanical analysis and broadband dielectric spectroscopy have been used to determine the glass-rubber and subglass transition properties of the polyimide [18-21]. Typically, three relaxation processes are observed with increasing temperature designated γ , β and α , respectively, with α corresponding to the glass-rubber relaxation (T_g).

Here is presented the characterization of two polymer films derived from two poly(ether imide)s containing isopropylidene or 6F groups. The properties of these films, such as thermal and electrical behaviour have been evaluated with respect to their structure by using dynamic mechanical analysis and broadband dielectric spectroscopy.

Experimental part

Preparation of the polymer films

Poly(ether imide)s **1** (Figure 1) were prepared by thermal treatment of the corresponding poly(amic acid)s, which were synthesized by polycondensation reaction of 2,2-bis[(3,4-dicarboxyphenoxy)phenyl]propane dianhydride (**6HDA**) or 1,1,1,3,3,3-hexafluoro-2,2-bis[(3,4-dicarboxyphenoxy)phenyl]propane dianhydride (**6FDA**) with 4,4'-(1,3-phenylenedioxy)dianiline (**PODA**), in N-methyl-2-pyrrolidone as solvent, at a concentration of 10-15%. The viscous solutions of poly(amic acid)s were cast onto glass plates followed by evaporating the solvent and thermal imidization at 120, 160, 180, 250°C, each for 1 h. Flexible transparent films of poly(ether imide)s **1** were obtained, which were stripped off the plate by immersion in hot water for 2 h. Such films having a thickness in the range of 40-60 μ m were dried under vacuum at 100°C and used for different measurements.

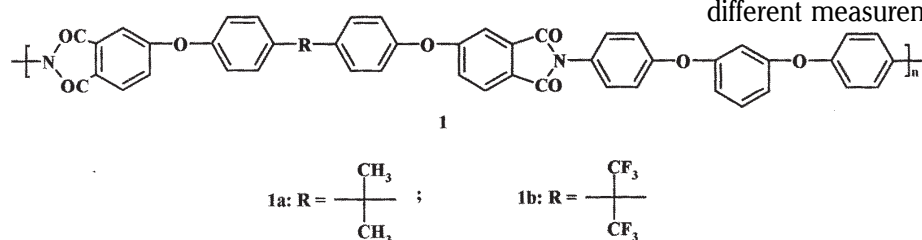


Fig. 1. Structure of poly(ether imide)s **1**

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Measurements

The inherent viscosities (η_{inh}) of the polymers were determined with an Ubbelohde viscometer, by using polymer solutions in N-methyl-2-pyrrolidone, at 20°C, at a concentration of 0.5 g/dL.

Thermogravimetric analysis (TGA) was performed on a MOM derivatograph (Hungary) in air, at a heating rate of 10°C/min. The initial decomposition temperature is considered the onset on the TGA curve.

The glass transition temperature (T_g) of the precipitated polymers was determined with a Mettler-Toledo differential scanning calorimeter DSC 12E. Sample size of 3 mg to 4 mg of each polymer was weighed in a crimped aluminum pan. The measurements were performed at a heating rate of 10°C/min, under a nitrogen purge of 50 mL/min. The mid-point of inflection curve resulting from the typical second heating was assigned as the T_g temperature of the respective polymers.

The dynamic mechanical analysis (DMA) was conducted using a PerkinElmer Pyris-Diamond DMA apparatus fitted with a standard tension clamps, at a frequency of 1 Hz. The sample was heated from -100°C to 300°C at 2°C/min, in a nitrogen atmosphere. The films (20x10x0.05 mm) were longitudinally deformed by small sinusoidal stress and the resulting strain was measured. The value of storage modulus E' , the loss modulus E'' and loss tangent ($\tan \delta = E''/E'$) were obtained as a function of temperature.

The dielectric measurements were carried out using a Novocontrol system composed of an Alpha frequency response analyzer and a Quattro temperature controller. The samples, prepared in the form of films with thickness of about 50 μm , were dried under vacuum at 100°C for 10 h. They were sandwiched between two copper electrodes of 20 mm diameter and placed inside temperature controlled sample cell. The complex permittivity: $\epsilon^*(f) =$

$\epsilon'(f) + i\epsilon''(f)$ has been determined in the frequency (f) range of 10^{-1} - 10^6 Hz and at temperatures ranging from -100°C to 175°C. The AC voltage applied to the capacitor was equal to 1.5 V. Temperature was controlled using a nitrogen gas cryostat and the temperature stability of the sample was better than 0.1°C.

Results and discussion

Poly(ether imide)s **1** were prepared by thermal treatment of the corresponding poly(amic acid)s which were obtained from **6HDA** or **6FDA** and **PODA**. The solutions of poly(amic acid)s in N-methyl-2-pyrrolidone were cast onto glass substrates and heated at different temperatures up to 250°C to yield thin films of poly(ether imide)s **1** having a thickness of tens of micrometers. The inherent viscosity values of the polymers **1a** and **1b** were of 0.61 dL/g and 0.54 dL/g, respectively.

The glass transition temperature (T_g) values of the polymers **1a** and **1b**, evaluated from DSC curve, were 188°C and 197°C, respectively (table 1). The thermogravimetric analysis showed that the poly(ether imide)s **1** exhibited high thermal stability, with insignificant weight loss up to 430°C (table 1).

Figure 2 presents the dynamic storage modulus E' and loss tangent $\tan \delta$ versus temperature, for polymers **1**. The polymers exhibited relaxation processes (α , β and γ processes) in their dynamic mechanical behaviour.

At very low temperature (around -64°C) a γ relaxation was observed in DMA analysis of polymer **1a**. This relaxation was not clearly seen in the DMA analysis of polymer **1b**.

At higher temperature a β relaxation process is observed in DMA analysis in the range from -40 to +150°C. The β relaxation occurs below the T_g and is associated with local bond rotations and short segments of chain motions along the polymer backbone. The magnitude of this relaxation is

Table 1
THERMAL PROPERTIES OF POLIMERS **1**

Polymer	T_g^a (°C)	T_g^b (°C)	IDT ^c (°C)	T_γ^d (°C)	T_β^e (°C)
1a	188	195	460	-64	55
1b	197	204	475	-	69

^a Glass transition temperature, determined from DSC curves; ^b Glass transition temperature, determined from DMA curves; ^c Initial decomposition temperature = onset of the TG curve; ^d Maximum γ transition temperature; ^e Maximum β transition temperature.

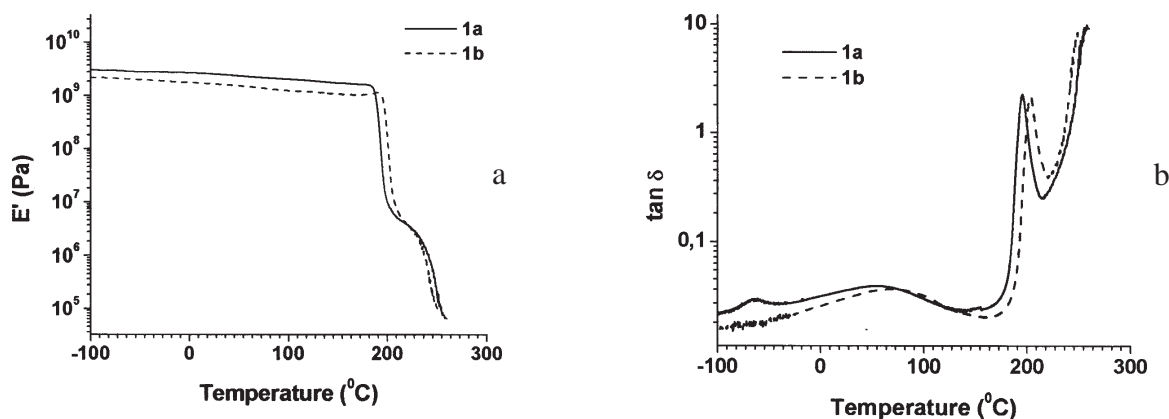


Fig. 2. Temperature dependence of (a) the storage modulus (E') and (b) $\tan \delta$, for polymers **1**

proportional to the concentration of segments contributing to the relaxation. The temperature value of the β relaxation maximum of polymer **1b** is higher than that of polymer **1a**. The introduction of 6F groups instead of isopropylidene groups increases the rigidity of the macromolecular chains thus increasing the temperature of β relaxation maximum.

The T_g values of the polymers **1** were also determined by DMA analysis. Storage modulus remained more or less constant up to 181°C (for polymer **1a**) and 191°C (for polymer **1b**), after which it sharply decreased in the T_g range. The polymer film exhibited a relatively narrow α -relaxation peak which corresponds to the T_g and reflects the onset of large scale chain motions. The T_g values determined by DMA measurements were slightly higher (195°C for polymer **1a**, and 204°C for polymer **1b**) when compared to those determined by DSC measurement [22].

Electrical insulating properties of polymer films **1** were evaluated on the basis of dielectric constant and dielectric

loss and their variation with frequency and temperature. Figure 3 presents the dependence of real and imaginary parts of complex permittivity on frequency, for polymers **1**, at three chosen temperatures. From figure 3 it can be seen that ϵ' slightly decreases when increasing frequency. The dielectric constant of polymers decreased gradually with increasing frequency because the response of the electronic, atomic and dipolar polarizable units varies with frequency. Polymers **1** exhibited low dielectric constant over the entire range of frequencies (10^{-1} - 10^6 Hz) even at 175°C. For many applications, dielectric materials with stable dielectric constant and dissipation factor values across large frequency and temperature ranges are highly preferred.

The dielectric constants for the polymers **1** at 0.1 Hz, 100 Hz and 10 kHz, at room temperature, are presented in

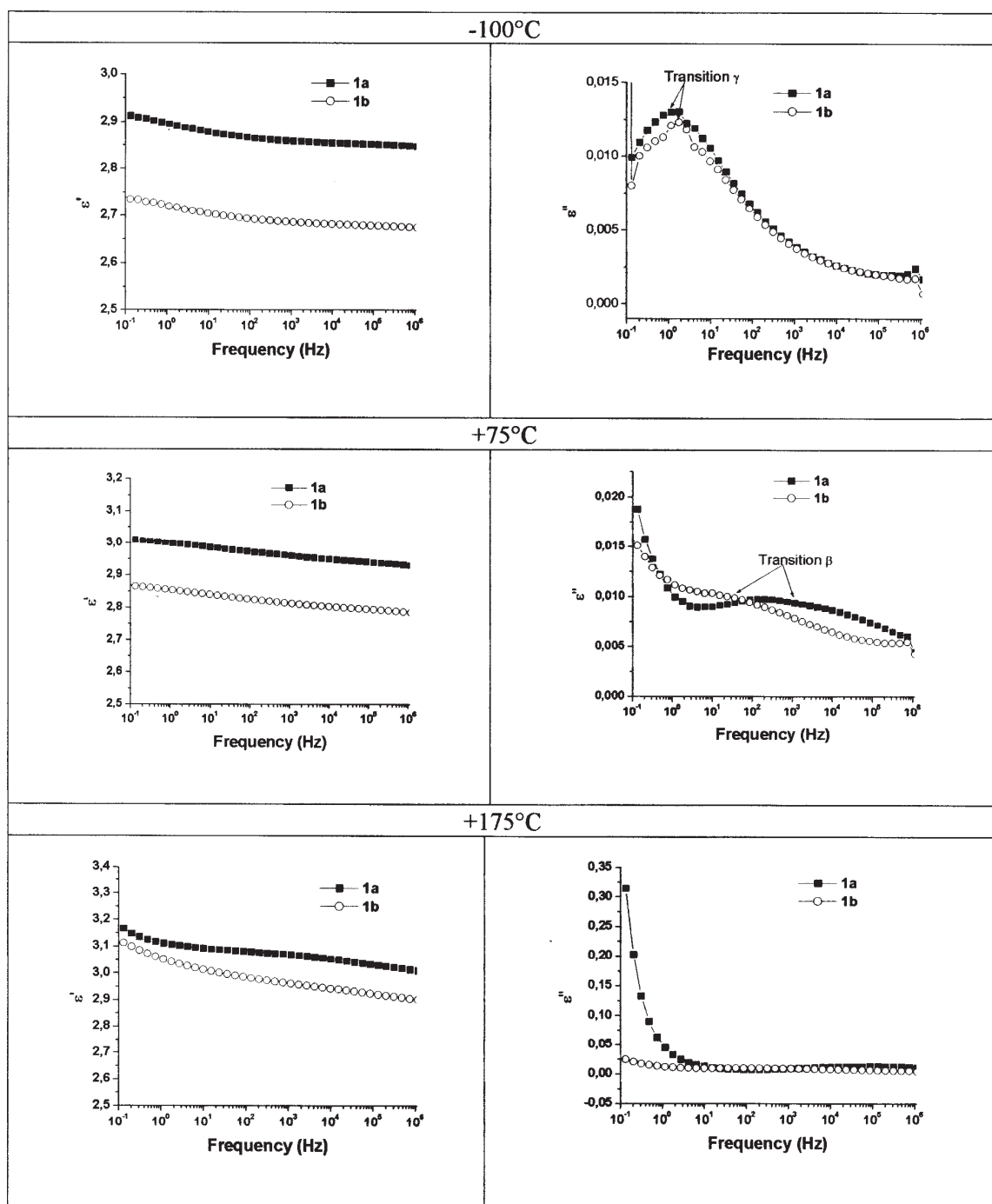


Fig. 3. Dependences of dielectric constant (ϵ') and dielectric loss (ϵ'') versus frequency, at different temperatures, for polymers **1**

Table 2
DIELECTRIC CONSTANT AT SELECTED FREQUENCY, AT 25°C, FOR POLYMERS 1

Polymer	Dielectric constant at			Ea of γ relaxation (kJ/mol)	Ea of β relaxation (kJ/mol)
	0.1 Hz	100 Hz	10 kHz		
1a	3.01	2.97	2.96	42.1	87.1
1b	2.85	2.81	2.80	42.9	81.2

table 2. The values of the dielectric constant at 10 kHz were in the range of 2.80-2.96. As it can be seen from table 2 these polymers exhibited lower dielectric constant values compared to an H-Film, a polyimide which is prepared from pyromellitic dianhydride and 4,4'-diaminodiphenylether and which is one of the most common polyimides used as dielectric in microelectronics applications, having a dielectric constant of 3.5 [3]. The polymer **1b** exhibited lower dielectric constant values than polymer **1a** due to the presence of 6F groups because of the less efficient chain packing and increased free volume that decreased the concentration of polar groups. In addition, the strong electronegativity of fluorine atoms results in very low polarizability of the C-F bonds, thus decreasing the dielectric constant [23-25].

The dielectric loss for polymer film **1a** at different temperatures taken in the range from 100 to 175°C is shown in figure 4. Two secondary β and γ relaxation processes, connected with local movements of polymer chain, appeared. Similar results were also obtained for polymer film **1b**. The activation map is the best way for a comparison of all samples and it is also necessary for the calculation of activation energy. Relaxation times (τ) of the secondary relaxation processes at the various temperatures have been determined from maxima position of ϵ'' at frequency scale. The activation plots are shown in figure 5.

The γ relaxation process is assigned to the small scale, local oscillations of imide rings [26]. The values of activation of γ relaxation for samples **1a** and **1b** were of 42.1 kJ/mol and of 42.9 kJ/mol, respectively, suggesting the existence of the same process for this transition.

The β relaxation process occurs below the T_g . About the β relaxation process there are many proposed explanations [27]. It was proposed that the main type of motion was a rotational vibration of small segments of a chain around quasi-equilibrium positions. The motion of phenylene and

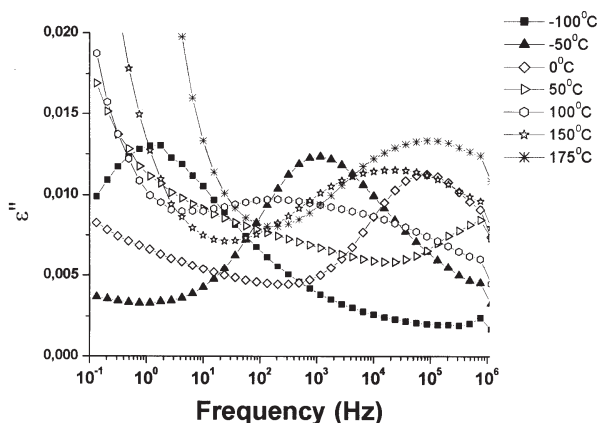


Fig. 4. Dependence of dielectric loss (ϵ'') versus frequency, at different temperatures, for polymer **1a**

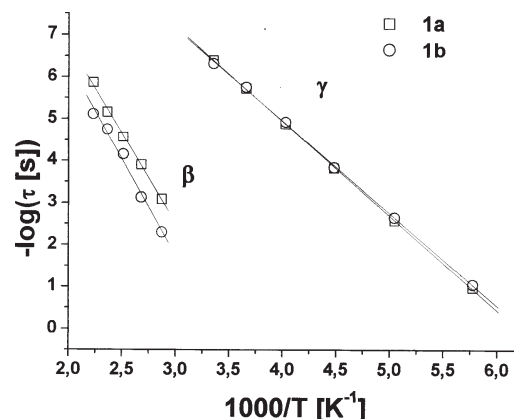


Fig. 5. Activation map for polymers **1**

imide rings contribute to the vibration [28]. It was also reported that β relaxation related with rotation of phenylene and imide groups around hinges such as ether linkages [29]. The values of activation energy of β relaxation were of 87.1 kJ/mol for polymer film **1a** and of 81.2 kJ/mol for polymer film **1b**.

Conclusions

Two poly(ether imide)s were prepared starting from an aromatic diamine containing ether linkages and two bis(ether anhydride)s having isopropylidene or hexafluoroisopropylidene groups. They could be easily processed into thin films by solution casting technique. The polymer films having the thickness in the range of tens of micrometers were flexible and resistant. Molecular relaxations were characterized in a broad temperature range by dynamic mechanical analysis and dielectric spectroscopy. The introduction of hexafluoroisopropylidene groups shifted the temperature of α -relaxation and β -relaxation to higher values. Two subglass transitions, γ and β , were evidenced by dielectric spectroscopy. The nature of the γ transition process was not influenced to a great extent by the presence of isopropylidene or hexafluoroisopropylidene groups, therefore the γ -relaxation activation energy was similar for these two polymers.

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