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A STUDY OF THE ELECTRICAL PROPERTIES AND SECONDARY TRANSITIONS OF POLY (ETHER IMIDE)

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Secondary transition temperatures of poly (ether imide) films were established below and above glass transition temperature, 220 ^{o}C by using inverse gas chromatography, dc conductivity-temperature and differential scanning calorimeter measurements. The secondary transition temperatures obtained these techniques were compared with the ones obtained by thermally stimulated depolarization current. Electrical characterization of the films having three different dopant concentration of 0.25 mol, 0.50 mol, and 0.75 mol per mol of polymer and the constant sample tickness of 6 μm was realized on the base of dc conductivity-temperature measurements. As doping concentration were increased, it was seen an increase at glass transition temperature.

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1. Introduction

Poly (ether imide) (Ultem) is an amorphous thermoplastic polymer with the structure as shown in Fig.1 that has interesting physical and chemical properties, being an attractive candidate for many technological applications [1, 2]. The ether units give a structure with flexible linkages and good melt flow characteristics. The aromatic imide units provide excellent heat resistance and high strength, and it is also resistant to hydrolysis and is capable of withstanding repeated autoclaving cycles. Thus, Ultem is ideal for high strength and high temperature applications, and also for applications requiring good dielectric properties over a wide frequency range. Because of its advantageous mechanical and electrical properties, it is suitable for industrial use, such as microwave devices, high performance electrical devices, and biomedical applications, in scientific products and in aerospace.

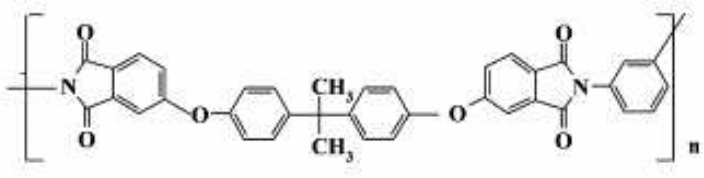

Fig. 1. The chemical structure of Ultem.

In this study, the electrical properties of Ultem films which can be used as semiconductor components have been studied for both undoped and doped samples. Measurements were realized by means of electrical conductivity. Morphological changes of the films are studied with scanning electron microscope (SEM), (JEOL mark, JSM-5410 LV). Then, Inverse gas chromatography (IGC),

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dc conductivity-temperature and differential scanning calorimeter (DSC) used to determine to the secondary transitions of Ultem [3,4,5,6]. IGC, dc conductivity-temperature and DSC are very fast and inexpensive techniques to determine the secondary transition temperatures of a polymer, in comparison to dynamic mechanical and dielectric analysis techniques. Therefore, the methods need lots of studies to confirm the reliability of these methods. Belena et al. [7] have observed that Ultem exhibits multiple secondary transitions by using thermally stimulated depolarization current (TSDC) measurements. In this study, we aimed to observe the secondary transitions of Ultem, by IGC, dc conductivity-temperature and DSC in order to establish the reliability of the method in determination of secondary transition temperatures.

2. Experimental

2.1. Inverse gas chromatography

Ultem and n-octane were a product of General Electric Corporation and Merck A.G. Inc, respectively.

A Hewlett-Packard 5890 Model, series II gas chromatograph with a thermal conductivity detector was used in this study. Data acquisition and analysis were performed by means of HP-3365 software. The flow rate of the carrier gas, Helium was kept below 6 cm^3 per minute, measured by a soap bubble flow meter. Chromosorb W-AW/DMCS were used as the support.

2.2. Electrical conductivity

Electrical characterizations of undoped and doped Ultem films were realized on the base of dc conductivity – temperature measurements together with its variation with doping ratio.

The measurements were carried out in 10^{-5}Torr vacuum and the dark. The electrical conductivity of the polymer was measured in Al / polymer / Al structure over the temperature range of -100 – 250^0C. It was performed on Ultem samples undoped and doped by BF_4^- in chloroform solution, 0.25, 0.50 and 0.75 mol dopant per mol Ultem, with thickness 6 μm.

Undoped and doped samples under study were prepared by dropping the polymer solution in chloroform with given concentration on Corning 7059 glass substrate thoroughly cleaned using analytical pipettes in air. Aluminum electrodes were deposited by vacuum evaporation at 10^{-6} Torr, along the length of the glass plates, at the width of 3mm, onto both surfaces of the samples to form a sandwich - type specimen for measurements of electrical conduction. Pogo contacts by direct pressure of on the aluminum electrodes were used to performe contact.

For the electrical characterization, dark conductivity of produced films were measured as a function of temperature using a home made liquid nitrogen vacuum cryostat having a thermocouple in good thermal contact with the sample. Samples were placed on top of a copper plate that is heated by a bolt heater embedded within. Temperature was recorded by Keithley DMM 196. Dark conductivity measurements were accomplished using a programmable Keitley 617 digital electrometer / voltage source interfaced to a computer.

The temperature dependence of conductivity was measured as the temperature being increased by 3 $^oC\ min^{-1}$. Organic film thickness was determined from the area formed by spreading polymer solution with known volume and concentration. The measurements were carried out in the dark.

2.3. Differantial scanning calorimeter

Perkin Elmer DSC6 was used in this study. DSC curves were obtained 10 mg samples, sealed in Aliminium pans, at several controlled heating reates.

3. Background

3.1. Inverse gas chromatography

The specific retention volume, per gram of the polymer in the chromatographic column, V_g^o, corrected to 0^oC is determined experimentally from inverse gas chromatography measurements as follows [8, 9]

$$V_g^o = Q\,(t_R - t_A)\,3/2\,[(p_i/p_o)^2 - 1] / [(p_i/p_o)^3 - 1]\,273.2 / (T_r\,w) \quad (1)$$

where Q is the carrier gas flow rate measured at the room temperature T_r; t_R and t_A are the retention times of the injected solvent and air, p_i and p_o are the inlet and outlet pressures of the carrier gas, respectively and w is the weight of polymer in the column.

3.2. Electrical conductivity

The type of electrical conductivity measurement involves a simple measurement of current as a function of time, temperature, ambient atmosphere and potential. Electrical conductivity varies exponentially with temperature as follows:

$$\sigma_D = \sigma_0 \exp(-E_a / kT) \quad (2)$$

where σ_D is the dark conductivity, E_a is the activation energy, and σ_0 the preexponential factor [10]. The conductivity is obtained by measuring the current flowing through a piece of the material and using the sample dimensions to calculate σ from the equation.

$$\sigma = (d / A\,V)\,I = G \times \text{Geometric factor} \quad (3)$$

where G (= I / V) is the conductance, d is the sample thickness, A is its area, and V is the potential across the material.

4. Results and discussion

The specific retention volume V_g^o of n-octane on Ultem obtained from Eq.1. was plotted as a function of the reciprocal of absolute column temperature in Fig.2 using retention-time measurements.

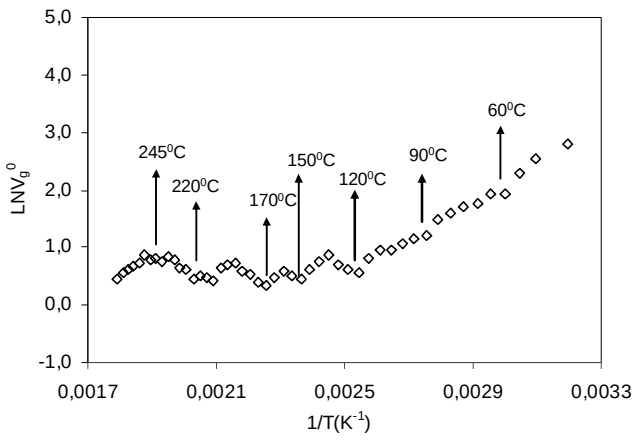


Fig. 2. The retention diagram of n-octane on Ultem.

The first deviated point from linearity of the all figures was accepted as a secondary transition temperature of the polymer. These transition are usually labeled with Greek letters, $\alpha(T_g)$, β, γ and so on. From the Fig. 2., the glass transition temperature α- (T_g) of Ultem was found to be 220 ^oC and five β-transition temperatures of the polymer below α- and one ρ-transition temperature above α-, were accepted as 170, 150, 120, 90, 60 and 245 ^oC, respectively.

Electrical characterization of the films was realized on the base of dc conductivity-temperature measurements for the undoped and doped films [11]. Fig. 3. shows the temperature dependence of dark conductivity (σ_D) of the undoped and doped samples. Undoped sample exhibit a dark conductivity $\geq 5.10^{-15}\ \Omega^{-1}cm^{-1}$ and doped films $\geq 10^{-14}\ \Omega^{-1}cm^{-1}$ at room temperature (RT).

Dark conductivity increases with temperature from $5.10^{-15}\ \Omega^{-1}cm^{-1}$ at RT to $10^{-13}\ \Omega^{-1}cm^{-1}$ at 240 ^oC for undoped films. It appears that the general behaviour of the conductivities are that σ_D increases in an activated way up with increasing temperature. An increase was obtained on the conductivity by doping up to one order of magnitude at room temperature and 240 ^oC.

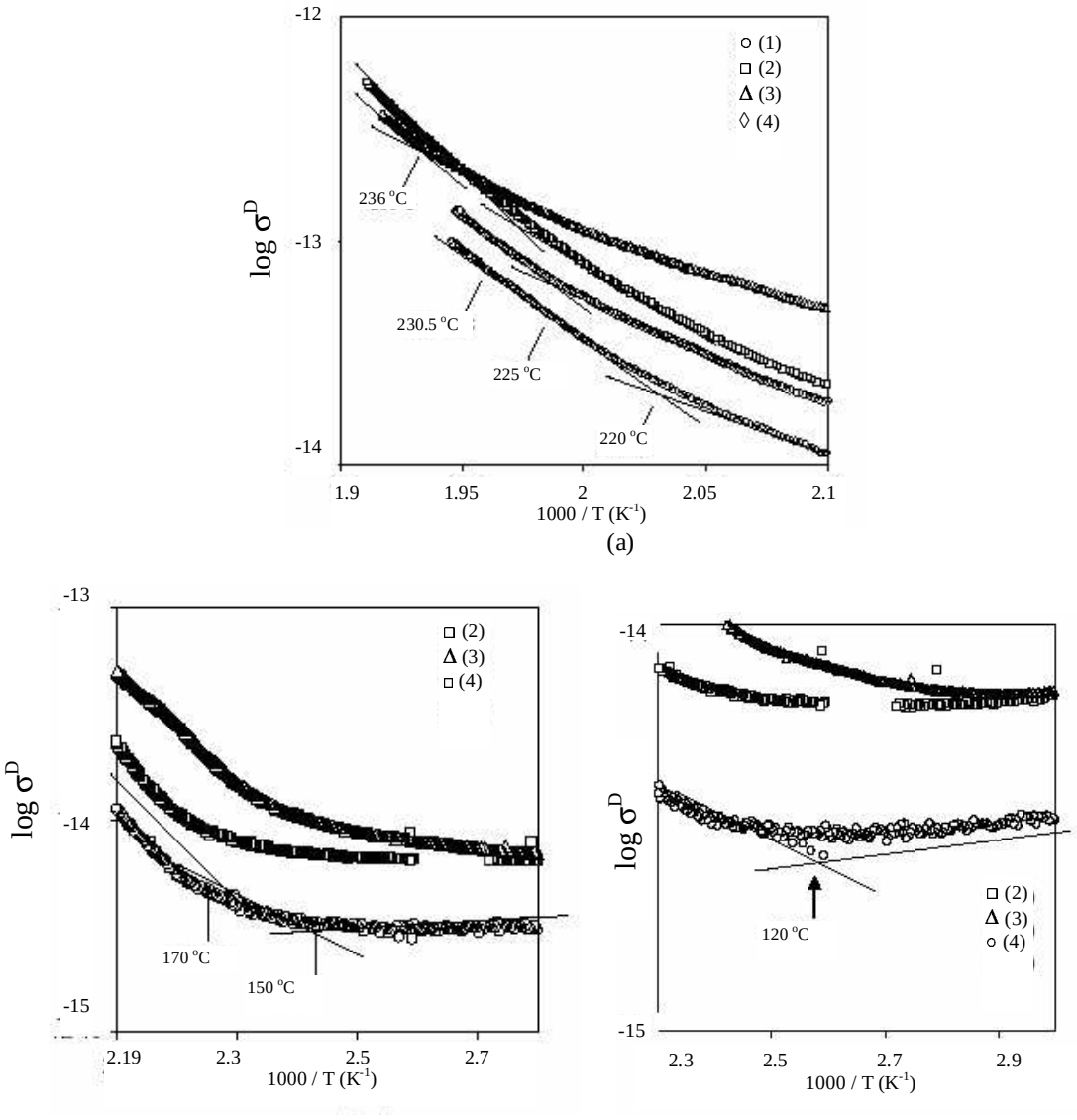


Fig. 3. Arrhenius plot of the conductivity of Ultem film: undoped (4), 0.25 mol/mol polymer (1), 0.5 mol /mol polymer (2) and 0.75 mol /mol polymer (3) doping ratio at different temperature ranges.

From conductivity measurements for undoped film, it was determined three β-transition temperatures of the polymer below α- were accepted as 170, 150, 120 ^{o}C, respectively.

It is shown Fig. 3 that as doping concentration were increased, an increase was seen at glass transition temperature as 220 ^{o}C for undoped and 225, 230.5 and 236 ^{o}C for doped films having 0.25 mol, 0.50 mol and 0.75 mol per mol of polymer, respectively and with the constant sample thickness of 6μm. This may be attributed to the specific interactions between polymer and dopant.

From the Fig. 4, it was determined three β- transition temperatures of the polymer below α-, were accepted as 127, 90, 70 ^{o}C, respectively.

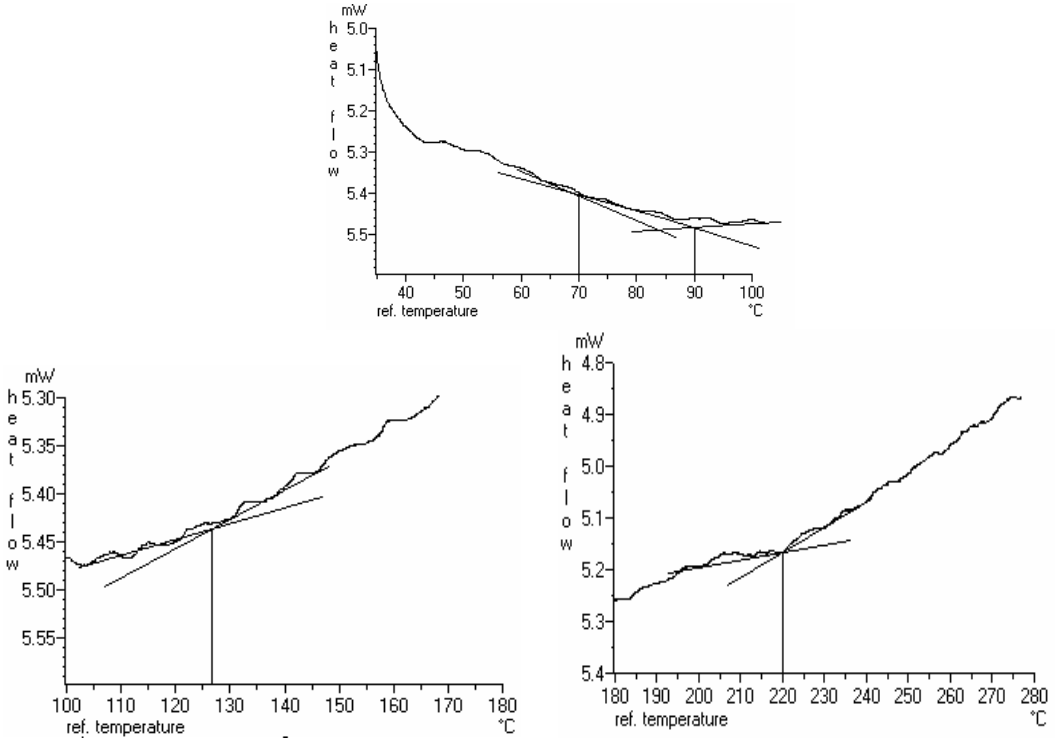


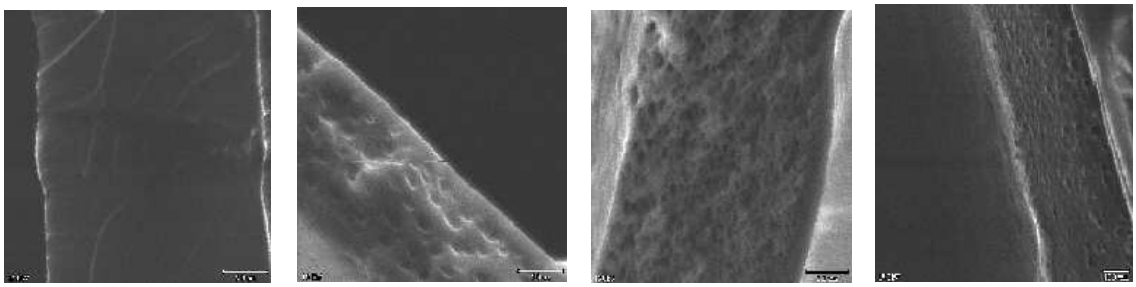
Fig. 4. The DSC thermogram of undoped Ultem film divided to three temperature ranges.

All transition temperatures observed in this study is compared with the value given by Belena et al. in Table 1. All results found in this study by inverse gas chromatography and electrical conductivity measurements and DSC are in good agreement with those observed by literature [7]. Some transitions could not be observed by DSC and electrical conductivity measurements. Therefore, these results suggest that the secondary transitions can be found more sensitively by IGC than dc conductivity-temperature and DSC.

Table 1. Comparison of the secondary transitions determined in this study with literature.

Secondary Transitions	Inverse gas chromatography t (^{0}C)	Electrical measurements t (^{0}C)	DSC t (^{0}C)	Literature [7] t (^{0}C)
γ	-	-	-	-123
β_5	60	-	70	70
β_4	90	-	90	90
β_3	120	120	127	-
β_2	150	150	-	152
β_1	170	170	-	-
α	220	220	220	225
ρ	245	-	-	244

SEM pictures of doped and undoped Ultem films with the dopant concentration of 0.25 mol, 0.50 mol and 0.75 mol per mol of polymer were given in Fig. 4. At Fig. 4(a), the undoped film indicates a rigid morphology. It seems that the rigidity of the polymer samples are decreasing with the dopant concentration.



(a) 5um (b) 5um (c) 5um (d) 10um

Fig. 4. SEM pictures of undoped (a) and doped Ultem films with the dopant concentration of 0.25 mol (b), 0.50 mol (c) and 0.75 mol (d) per mol of polymer.

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