DETERMINATION OF GLASS TRANSITION TEMPERATURE OF A POLYARYLATE BY USING BOTH INVERSE GAS CHROMATOGRAPHY AND ELECTRICAL CONDUCTIVITY MEASUREMENTS

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The glass transition temperature of a polyarylate was found from the slope changes of the logarithms of specific retention volume as well as electrical conductivity with reciprocal absolute temperature plots. The glass transition of the copolyester of bisphenol-A with terephthalic acid and isophthalic acid (50/50) Ardel®D-100 was determined as 463 K on the retention diagram for n-butyl acetate and n-octane obtained between 393 and 513 K by inverse gas chromatography. Electrical characterization was realized on the base of dc conductivity-temperature measurements for the films having three different thicknesses being 10.00, 5.00 and 2.50μm. The measurements were carried out in vacuum and dark. The electrical conductivity of the polymer was measured in Al/polymer/Al structure over the temperature range of 300 – 520 K. The activation energies of the samples were determined depending on the sample thickness. The glass transition temperature of Ardel®D-100 were found as 466 K with an average value of three film samples from conductivity measurements.

1. Introduction

The study of the properties of metal-insulator-metal structures with non-conductive polymers has started only recently [1] while these structures based on inorganic dielectrics have been studied for a long time [2]. Polymeric materials either organic or inorganic [3,4] are well known as insulating materials suitable for many industrial applications such as coatings, adhesives, covers, fibers,...etc. Even conducting polymers in their intrinsic nature are insulators but can be transferred to conductors by suitable doping with strong acceptor and donor agents [5].

Polyarylates are aromatic polyesters consisting of aromatic diols and dicarboxylic acid. The copolyesters prepared from bisphenol-A, terephthalic acid and isophthalic acid (Ardel®D-100) are amorphous and a representative example of polyarylates belonging to a class of engineering plastics:
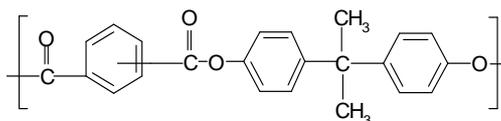

Fig. 1. The chemical structure of ARDEL®D-100.

They are characterized by their relatively high glass transition temperatures (T_g), resistance to UV and inherent flame retardance. When Ardel®D-100 exposed to UV light, it undergoes a molecular

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rearrangement resulting in the formation of protective layers that essentially serve as a UV stabilizer. This UV stability combined with superior retention of optical and mechanical properties make polyarylate an ideal choice for any application where weathering effects could pose a problem [6].

Ardel®D-100 has good wheathering properties, toughness and excellent flexural recovery. It can be used as semiconductor components and snap lock connectors. These polyesters are expected to find applications in transportations (interior panels for buses and aircrafts), glazing parts (solar collectors and appliances) and other optical uses.

In this study, Ardel®D-100 films have been studied. Measurements were realized by means of the inverse gas chromatography and electrical conductivity.

Inverse gas chromatography (IGC) technique which is simple, rapid and inexpensive [7] has been widely used in determining polymer properties such as T_g and polymer solvent interactions etc. Above T_g, the macromolecular segments become mobile and free volume fraction in the polymer increases [8, 9]. Polymer stationary phases exhibit unusual retention characteristics in vicinity of their glass transition temperature. Instead of the normal linear variation of the logarithm of the retention volume with reciprocal of absolute column temperature, generally a z- shaped retention diagram is recorded. One such diagram is characterized by an increase in retention volume with temperature. T_g is found as the first point deviated from linearity on the retention diagram [10,11].

Electrical characterizations were based on dc conductivity-temperature measurements and realized depending on the film thickness as well. It has been shown that T_g can be determined by using both the inverse gas chromatography technique and the electrical conductivity measurements.

2. Experimental

A. Inverse gas chromatography

Ardel®D-100, a trademark of polyarylate was a product of Amoco Corp. n-butyl acetate (nBA), n-Octane(O) were analytical reagent grade and used without further purification. 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. The proportion of polymer on the support was determined as 8,69 % by calcination. The column was stainless steel tubing with 3.2 mm o.d. and 1 m in length. The column was conditioned at 503 K for 24 h.

B. Electrical conductivity

The 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 a width of 3 mm, onto both surfaces of the samples to form a sandwich - type specimen for measurements of electrical conduction. Contact has been performed by direct pressure of pogo contacts on the aluminum electrodes.

The dark conductivity of produced films were measured for the electrical characterization, 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 taken between 300-520 K. The measurements were accomplished using a programmable Keitley 617 digital electrometer / voltage source interfaced to a computer.

The measurements were carried out in 10^{-3} Torr vacuum and the dark. The temperature dependence of conductivity was measured at constant electrical field 40 kVcm^{-1} with the temperature being increased by 3 Kmin^{-1}.

Thicknesses of the Ardel®D-100 films studied were 10.00, 5.00 and 2.50 μm. Organic film thickness was determined from the area formed by spreading polymer solution with known volume and concentration.

3. Background

A. Inverse gas chromatography

The specific retention volume, V_g^o is determined experimentally from inverse gas chromatography measurements as follows [12, 13]

$$V_g^o = Q \, (t_R - t_A) \, J \, 273.2 \, / \, (T_r \, w) \tag{1}$$

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, respectively, w is the weight of polymer in the column and J is the pressure correction factor which is calculated from the equation:

$$J = 3/2 \, [\, (p_i / p_o)^2 - 1] \, / \, [(p_i / p_o)^3 - 1] \tag{2}$$

where p_i and p_o are the inlet and outlet pressures of the carrier gas, respectively. Thus, specific retention volume of a solvent is the volume of the carrier gas, measured at 273.2 K and corrected for column pressure drop, which will elute the solvent vapor from the column containing 1 g of the polymer as a stationary phase.

B. 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, is a function of time, and may vary with electrical field: i.e.,

$$\sigma_D = \sigma_0 \, \exp \, (- E_a / kT) = f(time) = A \, f(E) \tag{3}$$

where σ_D is the dark conductivity, E_a is the activation energy, and σ_0 the preexponential factor [14]. 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.

$$\sigma = (d / A \, V) \, I = G \times \text{Geometric factor} \tag{4}$$

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

V_g^o of nBA and O on Ardel®D-100 obtained from Eq. 1. and Eq. 2. was plotted as a function of the reciprocal of absolute column temperature in Fig. 2. using retention-time measurements. According to the inverse gas chromatography theory, amorphous polymers show this type of characteristic retention diagram indicating their structure [10, 15]. From the retention diagram, T_g was found to be 463 K as the point from which the deviation from linearity was first seen as the temperature increases in Fig. 2.
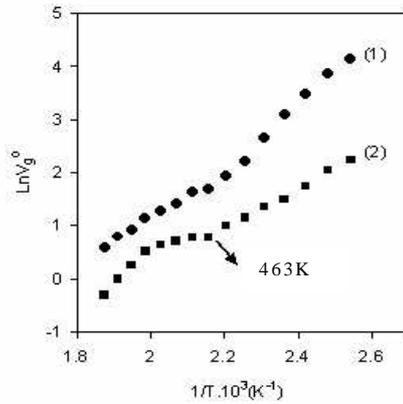
Fig. 2. The retention diagram on Ardel®D-100 of nBA (1) and O (2).

For the electrical measurements, different voltages were applied on each sample so as to keep the applied field constant at E = 40 kV.cm^{-1}. Fig. 3 shows the current-voltage characteristics of 10 μm thick sample. Current in this region obeys Ohm's law and governed only by the resistance of the polymer material and controlled by thermally generated carriers.
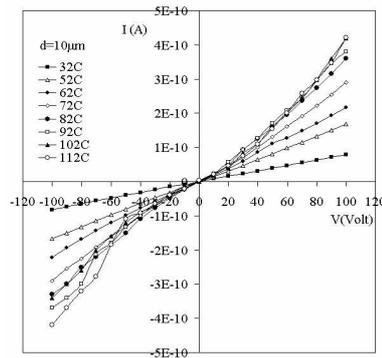

Fig. 3. I-V characteristics of Al–polymer–Al (thickness 10μm) structure at different temperatures.

Fig. 4 shows the temperature dependence of dark conductivity (σ_d) of the Ardel®D-100 having different thicknesses. All Al–polymer–Al structures exhibit a higher dark conductivity than $5.10^{-16} \Omega^{-1} cm^{-1}$ at room temperature (RT).

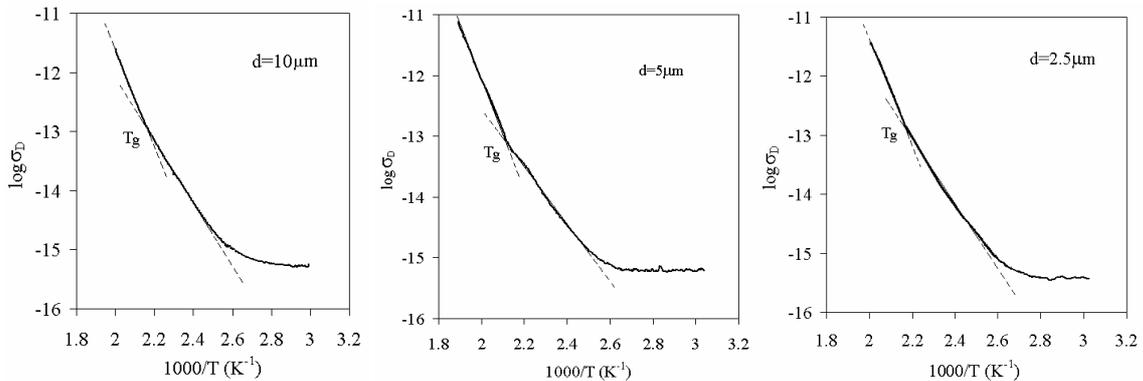Fig. 4. Arrhenius plot of conductivity for the Al–polymer–Al structure at E=40 kV.cm^{-1} with different thicknesses of 10 μm, 5 μm and 2.5 μm films.

In Fig. 4, it appears that the general behaviour of the conductivities are that σ_d increases in an activated way up almost five order of magnitude with increasing temperature. In other words, dark conductivity increases with temperature from 5.10^{-16} $(\Omega cm)^{-1}$ at RT to 10^{-11} $(\Omega cm)^{-1}$ at 520 K. T_g of Ardel$^{\circledR}$D-100 was found to be average 466 K at the point of the changes of the slopes of the conductivity in the temperature range studied. A considerable conductivity changes started after T_g [16].

We calculated also the activation energies of the films below and above T_g. Fig. 5 shows the determined activation energy values from Fig. 4, depending on the film thickness. As it can be seen from Fig. 5, the activation energies (E_{a1}) from first branch (466-520 K) and (E_{a2}) from second branch (300-466K) of the Fig. 4, did not changed remarkable depending on the sample thickness. The activation energy was found around $1.6 \pm 0.1eV$ and $1.0 \pm 0.1eV$ above and T_g, respectively.
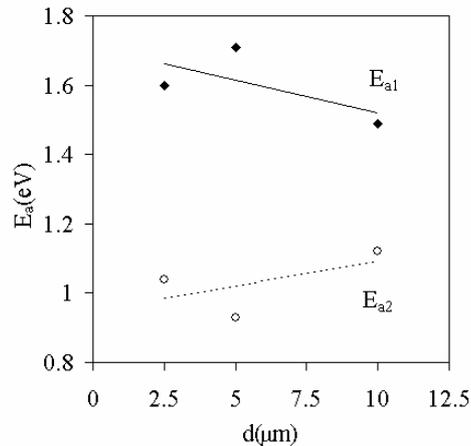

Fig. 5. Activation energies as a function of film thickness, calculated from Fig. 4.

4. Conclusion

We have measured the dark conductivity of the Ardel$^{\circledR}$D-100 depending on the temperature. The electrical characteristics of the samples prepared by cast method was investigated in the temperature range of 300-520 K. Dark conductivities increased five order of magnitude at the temperature range studied. The changes on the conductivity have been almost parallel to one another throughout the temperature range studied for all films having different thicknesses.

Activation energies for conductivity of the polymer were calculated from the slopes of linear branch of the plots in the Fig. 4. We observed that the rate of increase of conductivity with reciprocal of absolute temperature of the polymer changes at T_g. By using this phenomenon, we determined the T_g of Ardel$^{\circledR}$D-100 as 466 K which is in agreement with 463 K found by IGC. We did not observed any remarkable change on T_g with the sample thicknesses. As a result, this study suggest that the electrical conductivity measurements depending on the temperature can be use to determine T_g of a polymer.

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