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Electrical characteristics of thermally stable polyurethanes with high glass transition temperatures

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The resistivity of the synthesized polyurethanes with high glass transition temperatures was measured at different feed concentrations of monomers namely, 4-[bis(2-hydroxyethyl) amino]-4'-nitroazobenzene and N-phenyldiethanolamine to establish the correlation between resistivity and monomeric units. The results suggested that resistivity increases with the increase in feed concentration of 4-[bis(2-hydroxyethyl) amino]-4'-nitroazobenzene. The measurements were also performed on polyurethane samples at different thickness, indicating the decrease of resistivity with film thickness. The effect of temperature on resistivity has also been observed below their glass transition temperature, determined by differential scanning calorimetery.

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1. Introduction

Recent studies [1-3] have shown the polymeric materials to be promising insulator for many industrial applications. Conducting polymers have been reported to be insulator in their intrinsic nature but their transformation in conductors is possible by suitable doping with strong acceptor and donor agents [4]. Polymeric materials, depending on their conductivity, can be used in numerous end-use applications. Poor conductivity polymers are widely used as insulating wire coatings. For some applications, however, poor conductivity leads to undesirable consequences-specifically the tendency to build-up and retains static electrical charges. By coating an insulator with a very thin layer of conducting polymer, it is possible to prevent the build up of static electricity.

Therefore, it is basic necessity to understand the factors affecting the electrical conductivity [3,5] of these polymeric materials. However, the conduction mechanisms in polymeric materials have always been a challenge for the researchers, but the results obtained describe to some extent the charge carrier migration and its variation with different parameters. The direct analytical measurements fail sometimes to justify the expected conduction mechanism because of low currents. To overcome this problem, different measurement techniques such as resistivity measurements using four-probe and thermal treatment of the samples are employed to study the relationship between their electrical properties and chemical structure.

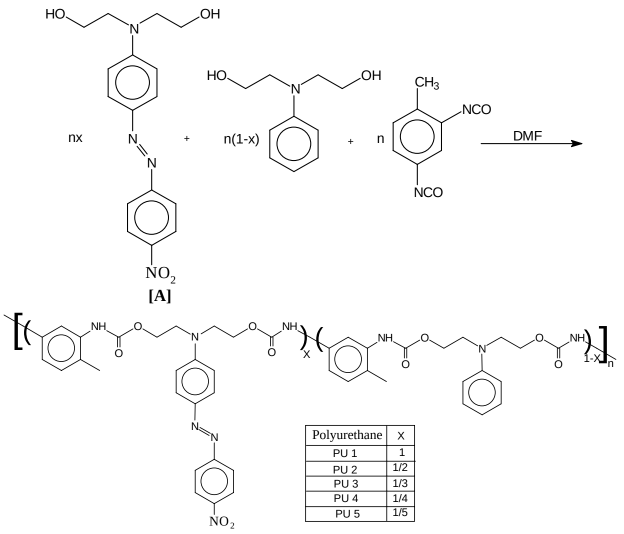
In the present study, polyurethanes with different feed concentrations of the monomers 4-[bis(2-hydroxyethyl) amino]-4'-nitroazobenzene and N-phenyldiethanolamine have been used because of their high thermal stability and high glass transition temperatures. The electrical properties of polyurethane thin films deposited by resistive heated vacuum evaporation have been measured. Electrical characterizations were realized on the basis of dc resistivity with temperature variations. The type of electrical conductivity (resistivity) measurements being reported involves a simple measurement of current as a function of voltage and temperature. Attempts were then made to relate the resistivity to feed concentration of monomeric units in polyurethane system.

2. Experimental

The synthesis of chromophore namely, 4-[bis(2-hydroxyethyl) amino]-4'-nitroazobenzene and polyurethanes has been described in our earlier paper [6]. Molecular masses of the polymers were calculated against polystyrene standard using tetrahydrofuran (THF) as the solvent. Differential scanning calorimetery (DSC) and thermogravimetric analysis (TGA) were performed under nitrogen atmosphere at a heating rate of 10 °C/min. on Perkin Elmer Pyris-I apparatus and Perkin Elmer (Pyris Diamond) thermal analyzer respectively. Thin films of these polyurethanes with thickness of the order of 1000 Å were grown on the cleaned quartz glass slides by resistive heated vacuum evaporation technique at a vacuum of 10^{-6} mm/Hg with the help of high vacuum coating system (NIRVAT EU-300). The thickness of the thin films prepared was controlled with the help of thickness monitor. The resistivity measurement was performed on the prepared samples by four-probe technique [7]. The band gaps for the polymeric materials have been measured [8] using UV/visible absorption spectroscopic technique.

3. Results and discussion

The synthesis of the polyurethanes with different feed concentrations of monomers namely, 4-[bis(2-hydroxyethyl) amino]-4'-nitroazobenzene **[A]** and N-phenyldiethanolamine are shown in Fig. 1.



Polyurethane	X
PU 1	1
PU 2	1/2
PU 3	1/3
PU 4	1/4
PU 5	1/5

Fig. 1. Synthesis of polyurethanes.

Polyurethanes PU1-PU5 were prepared by condensation polymerization of varying concentrations of monomer 4-[bis(2-hydroxyethyl) amino]-4$'$-nitro-azobenzene **[A]** and N-phenyldiethanolamine with 2,4-tolylenediisocyanate. These polyurethanes can be used for high temperature applications because of their high thermal stability and high glass transition temperatures (Table 1) as suggested by thermal analysis techniques.

Table 1. Physicochemical properties of polyurethanes.

Polymers	X	Weight-Average MolecularWeight (Mw)	Polydispersity index (PDI)	T_g [a] (°C)	T_d [b] (°C)	Band gap (eV)
PU1	1	4910	1.98	-	233	2.62
PU2	1/2	5350	1.94	230	255	2.32
PU3	1/3	5540	1.95	234	257	2.28
PU4	1/4	5700	1.87	241	258	2.21
PU5	1/5	5880	1.88	245	260	2.15

[a] Glass transition temperature determined by DSC

[b] Decomposition temperature determined by TGA

In this study, the effect of feed concentrations of monomers, temperature and film thickness on resistivity has been described. Fig. 2, showing variation of resistivity with feed concentrations at room temperature, reveals that resistivity increase with increase in concentration of 4-[bis(2-hydroxyethyl) amino]-4$'$-nitroazobenzene.

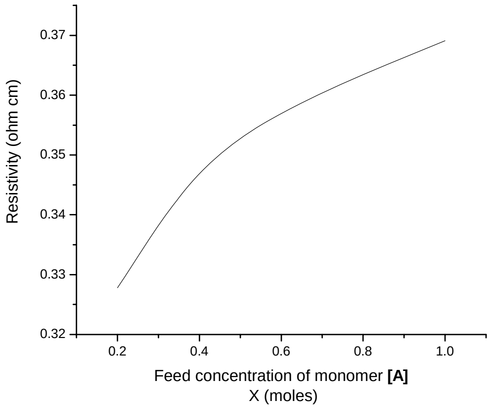


Fig. 2. Effect of feed concentration of monomer on resistivity of polyurethane thin films (thickness 100 nm) at room temperature.

It may be explained on the basis that as the feed concentration increases, the grain boundaries and hence the resistivity increase.

Fig. 3 shows the temperature dependence of resistivity for polyurethane thin films (as an illustration, curves for PU1, PU3 and PU5 are shown only) of thickness 100 nm.

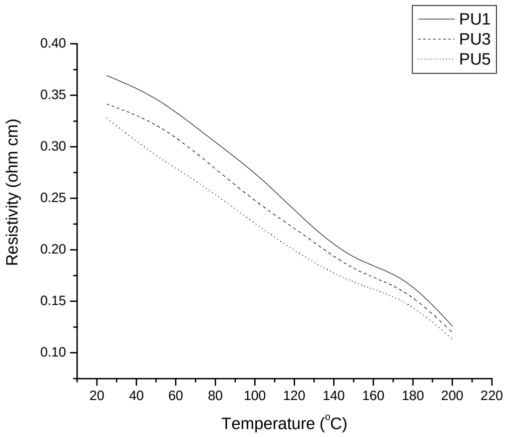


Fig. 3. Temperature dependence of resistivity of polyurethane thin films with thickness 100 nm.

It is evident from the Fig. 3 that increase in temperature leads to decrease in resistivity. The increase in temperature increases energy of the electrons getting more electrons into the conduction band, thus making more free electrons available, which increases the conductivity and hence decreases the resistivity.

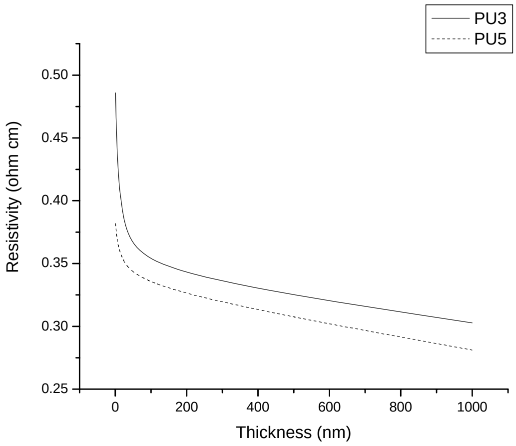


Fig. 4. Variation of resistivity of polyurethane thin films with thickness.

The variation of resistivity of polyurethane thin films with thickness is shown in Fig. 4. As the thickness increases, the resistivity decreases which can be attributed to the fact that the thin films deposited are rough and hence more surface area and scattering leads to higher resistivity. Therefore, roughness decreases with thickness and hence resistivity decreases.

4. Conclusions

The correlation between resistivity and feed concentration of monomeric units in polyurethanes has been estabilished which suggested that resistivity increases with increase in concentration of 4-[bis(2-hydroxyethyl) amino]-4$'$-nitroazobenzene. The variation in the resistivity with feed concentration of monomer as in Fig. 2 is as per the expected results in accordance with the Table 1, which shows the energy band gaps of different polyurethanes. The temperature dependence of resistivity has been measured from ambient temperature to 200 ºC (below T_g). The resistivity was found to increase with increase in film thickness.

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