Summary

SUMMARY

Polymer complexes have received a considerable attention in the last decade. Kinetics, elucidation of the structures and thermal stabilities have been of particular interest.

The present work is concerned with the preparation, characterization and studying the electrical properties of some polyesters and their complexes. This work includes three chapters, the first chapter embraces the introduction which showed some aspects about the published studies concerning the different preparation methods of polymers and their metal complexes and some views about the electrical properties of the polymeric complexes. The second chapter includes the experimental part, which describes the materials, and instruments, which have been used. It includes also the synthetic method for preparing the polymer complexes which involve the reaction of aspartic acid with each of the following dioles, namely: 1,6 hexane diole to form polyhexamethylene aspartate (PHMA), diethylene glycol to form polydiethylene aspertate (PDEA), propylene glycol to form poly-propylene aspartate and dipropylene glycol to form polydipropylene aspartate (PDPA), followed by reaction of the above polyesters with chlorides of Pb(II), Ni(II), Cd(II), Cu(II), Co(II), Mn(II), Fe(III), Hg(II) and Mg (II) to form polyester-metal complexes. The polyester-double metals complexes by the reaction of PDPA with Ni(II) + Co(II), Ni(II)+ Cu(II) and Co(II)+ Cu(II) were also prepared.

The polyesters and polyester –metal complexes were characterized by IR & ^{1}HNMR spectral studies, thermal analysis (differential thermal analysis "DTA", thermal gravimetry "TG" and thermal mechanical analysis "TMA"), elemental analysis (C,H,N), atomic absorption and titration using EDTA. Also we studied electrical properties of PDPA and their double metals complexes including DC-, AC-electrical conductivity, relative permittivity (ε`) and dielectric loss mesasurments (ε″) over a wide range of temperature and frequency.

The metal ions were found to be six-coordinated with two water molecules as additional ligands besides oxygen and nitrogen atoms of polyesters repeating units. IR and elemental analysis indicate that all investigated polyesters PHMA, PDEA, PPA and PDPA reacts with the metal chlorides in a 2 : 1 (monomer : metal) molar ratio.

Thermo-gravimetric analysis (TGA) showed that, coordination polymers are thermally more stable than polyesters. By using the initial temperature of decomposition as a measure of the thermal stability it was found that the thermal stability of investigated polyesters increase in the order:

PDPA > PHMA > PDEA > PPA

and the thermal stability of metal –complexes increase in the order:

$- Pb^{2+}- > -Cd^{2+}-> - Cu^{2+}- > -Ni^{2+}- > -Co^{2+}-.$

The results showed that Tg values increase with increasing of molecular weight and ionic radius for investigated compounds. In contrast to that the ionization potential of the investigated metal ions showed non effect on the thermal stability of the investigated complexes.

In case of double metals complexes, the order of the thermal stability of the complexes with respect to metal ions is :

[Co(II) +Cu(II)] > [Cu(II) + Ni(II)] > [Ni (II) + Co(II)] > Ni(II).

From thermal mechanical analysis studies it was found that, the mechanical stability of the investigated polymers increases in the order: PPA> PHMA > PDPA > PDEA. Also it seems that, the thermal stability almost increases with decreasing the chain length of monomer and with increasing its branching.

The dielectric constant ∈` values for PDPA and its complexes refer to that these compounds can be classified as simple dielectric with a slightly ionic polarization. The polarization was found to increase with decreasing bond length between the polymer and the metal ions. The dielectric constant ∈` and dielectric loss ∈″ showed anomalous behaviour at temperatures coincide well with those found in electrical conductivity measurements.

At room temperature ∈` values was found to decrease in the order: PDPA-Ni(II), Cu(II) > PDPA-Co(II) > PDPA-Ni(II) > PDPA-Cu(II), Co(II) > PDPA-Ni(II); Co(II) > PDPA –Cu(II) > PDPA.

The electrical conductivity for PDPA and its complexes showed semicanducting behaviour at higher temperatures. Introducing metal ions in the polymer back bone (PDPA) improves its electrical conductivity in the order:

PDPA –Ni(II), Cu(II)> PDPA-Co(II)> PDPA-Cu(II) > PDPA – Co(II), Cu(II)> PDPA-Co(II), Ni(II) > PDPA –Ni(II) > PDPA.

It is suggested that the type of coordinated metal ions play an important role in the conduction process and the conduction pathway was assumed to be occurring in the complex via the ligand molecules.