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Synthesis and Characterization of Conducting Polymers and Their Composites*

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Blends of conducting polymers polypyrrole and polyaniline, in the insulating host polymers, polybisphenol A carbonate, polyamide and polyamide have been prepared electrochemically. Composite homogeneity and a possible chemical interaction between the host matrices and the conducting polymers were searched. Several spectroscopic and thermal analyses of free standing films suggest such an interaction.

The properties of intrinsically conducting polymers make them suitable materials for several applications. Electrochemical polymerization of some compounds on polymer-coated electrodes was yet another concern for realizing electrically conducting composites[1-4]. The main purpose is to obtain homogeneous blends which retain the characteristics of the two components. In the above mentioned technique polymerization starts around the interface between the electrode surface and the host polymer film coated on the electrode. The resultant conducting polymer (CP) grows inside the matrix forming an electrically conducting polymer alloy film. In obtaining low percolation thresholds several aspects such as H-bonding and/or grafting have been found to be valuable[5].

Polybishenol A Carbonate (PC) as the Host Matrix

The electrochemical polymerization of pyrrole in acetonitrile and aniline in aqueous media had been reported[5,6] on PC-coated Pt electrodes. The minimum conducting polymer content that yields a reasonable conductivity for the film blend was related to the threshold conductivity and miscibility arising from hydrogen bonding and/or other molecular interactions. In the case of PC/PPy left composite DSC studies revealed interesting results. Not only the Tg for PC was lost but another value (337°C) had appeared in the thermogram. In the thermal gravimetric analysis of the blend containing 11% PPy left a residue whose weight was 20% of the original blend. This observation suggests that PPy forms a strong complex with PC that is stable enough to resist the decomposition temperature of PC[5].

As to the polyaniline (PAn)-PC composite very similar results were obtained[6]. The electrolytic film showed several differences with respect to a simple mechanical mixture of the two polymers (PAn and PC) with a same composition as the composite film

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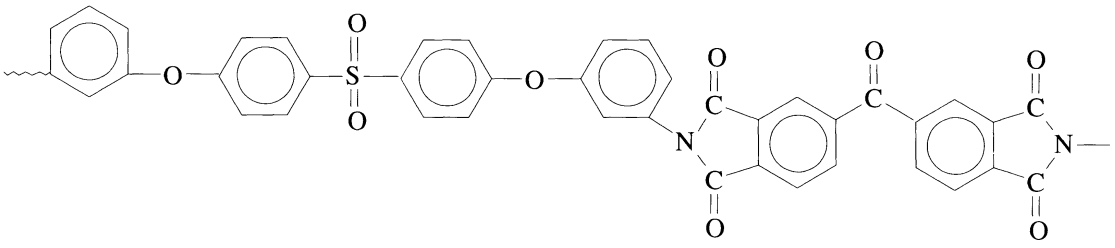
a) PC in the composite film was not any more suluble in chloroform, b) spectra of the mechanical mixture (MM) and PAn/PC were different, c) DSC thermograms of MM and PAn/PC have different characteristics, d) SEM micrographs interestingly reveal that the solution and electrode sides of the composite film were exactly the same contrary to Niwa's model[1]. This model proposes that electrochemical blending yields a composite which is rich in the conducting component on the electrode side even the majority of the film may be homogeneous, e) the gas sensing behaviors of pristine PAn and PAn/PC composite was found to be completely different[7]. The reproducibility and reversibility of the latter was perfect towards oxidizing and reducing gases (HCl and NH_3) in the sense that equal amounts of time was elapsed for resistance decreases and increases upon exposure. In addition, composite film response towards different concentrations of the gases (by volume) were linear as expected from a gas sensor, whereas the pristine PAn was not found to be dependable. The time required to reach the saturation point upon exposure to the gas for pure PAn was about 5 fold compared to the composite film.

These arguments suggest that there must exist a strong interaction between the insulating polymer (IP) and CP one of which can be a grafting of the PAn onto PC during synthesis.

Polyimide as the Host Matrix

The polyimide synthesized in Gebze Center of Turkish National Scientific Research Council were used as the host polymer for the synthesis of polypyrrole. The structure is given below:



The FTIR spectra of the electrolytic film (Figure 1a) is different than that of PI, PPy mechanical mixture. The conductivity of the resultant composite has almost the same value of pure PPy (0.1 S/cm) indicating that several sites has been added to the CP to enhance the hopping process although 50% of the film is composed of an IP.

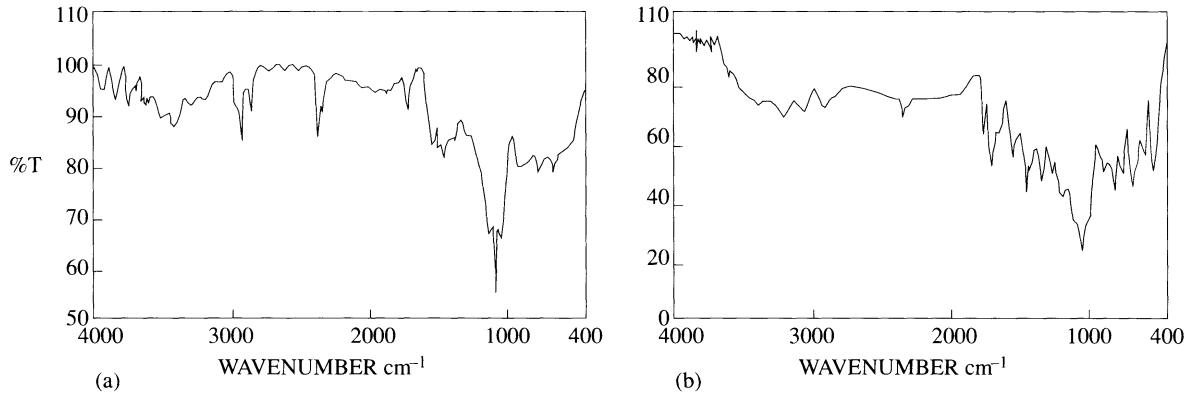


Figure 1. FT-IR spectra of A) PI/PPy film B) PI+PPy mixture (50% PPy content both)

Polyamide as the Host Matrix

Potentiostatic polymerization of Py were carried out using a polyamide (PA) (a linear C-20 amide) coated Pt electrode in a similar way to PPy/PC composite syntheses. The conductivity of the film was found to be within the same order of magnitude with pure PPy synthesized in the same manner (10 S/cm). The FTIR studies of the free standing film taken in KBr and in gas phase[8] clearly indicated that the resultant polymer was completely different species than a homogeneous mixture of polyamide and polypyrrole. Gas phase FTIR spectra of the composite at 350° C and 10^{-3} Torr has different features whereas the spectrum of a MM yields only the summation of PA and PPy spectra. TGA analyses reveal that the so-called composite has a single phase as denoted by a single weight loss pattern. Although the H-bonding (due to C=O of PA and N-H of Py) was clearly seen in the solid state FTIR spectra, those properties mentioned above can not explain such strong interactions. The DSC thermogram of the film shows a transition above 340° C while the MM has the Tg of PA only. Similar to PAn/PC polymers PA/PPy composite has very responsible and

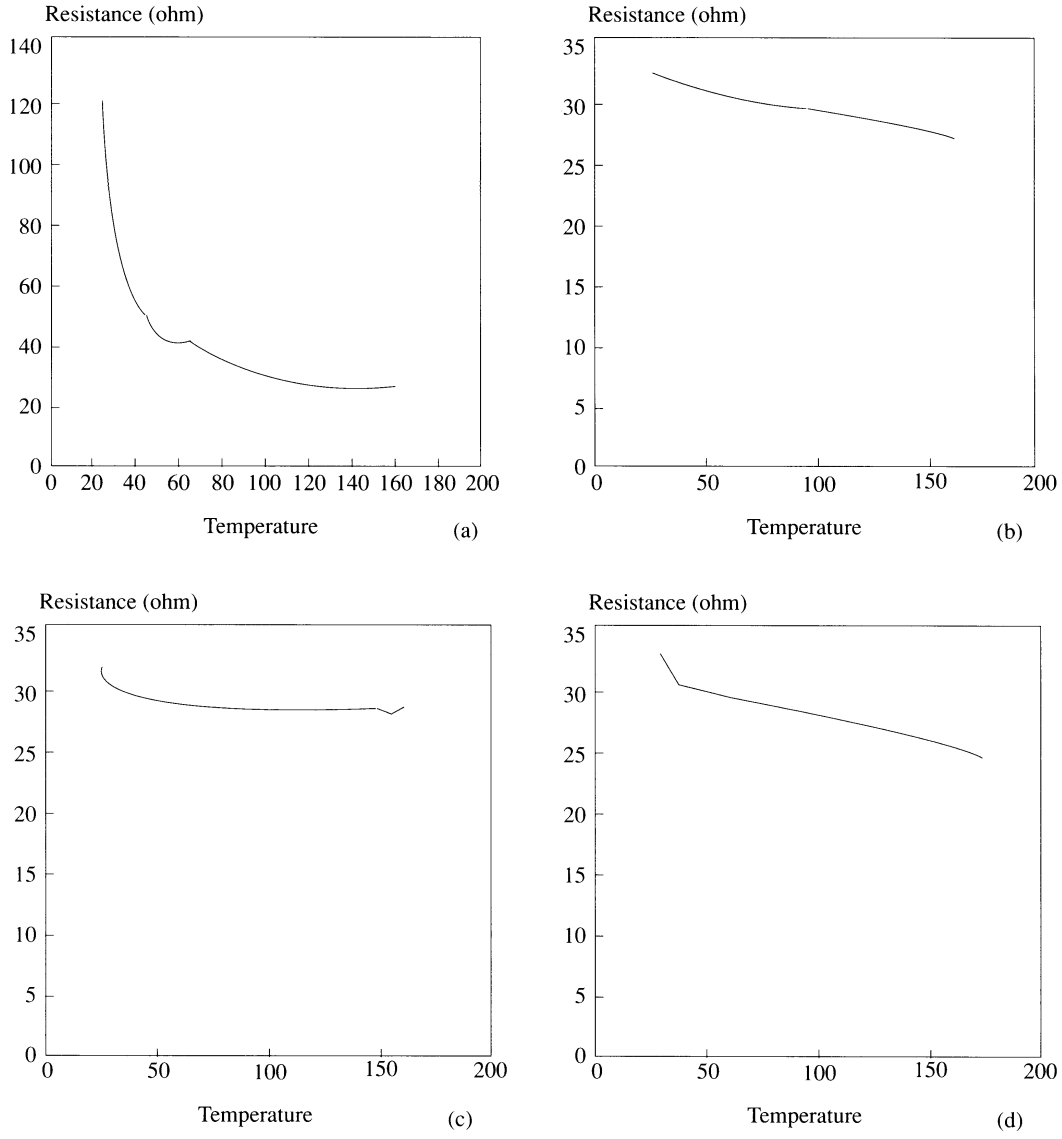


Figure 2. Results of resistance changes of pure PPy against temperature a) First heating; b) first cooling; c) second heating; d) seconding cooling

reversible behavior towards NH_3 and HCl gases. The thermal dependence of PPy and the composite had also been examined. Figure 2 shows a set of heating and consecutive cooling processes for pure PPy. During first heating at the first 5 °C resistivity of PPy decreases to 2/3 of the initial value. Figure 3 shows the response of composite film to heat. After the first heating there exists a more pronounced reversibility compared to pure PPy. The resistance of composite film decreases to 3/8 of its initial value in 5 °C during first heating until 55 °C the sharp decrease continues and thereon there is a slow decrease. The same trend was observed for other composites which have different PPY contents. The pyrolysis mass spectrometer studies on PA/PP, PA, PPy and MM shows that PPy decomposes to its monomer and n-hexane[9]. Pyrolysis products of the MM give the same features as the pure PPy and PA. On the other hand, the film yields a spectra indicating a possible chemical interaction between the polymers although the structure has not been identified yet.

The preliminary ESCA work on these composites[10] has indication of a chemical binding between the carbonyl carbon of PA and pyrrole nitrogen although further studies are required for a solid proof.

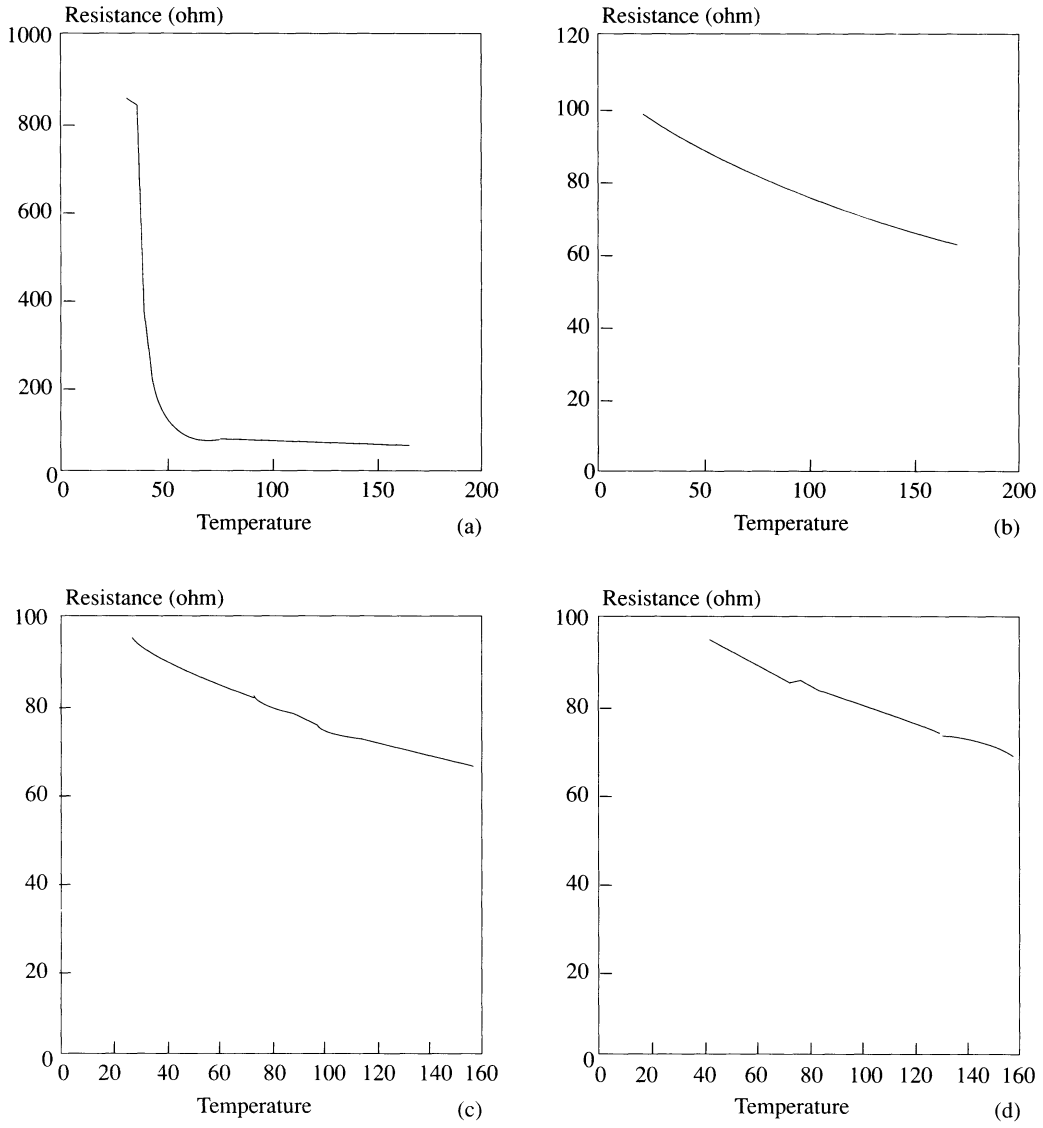


Figure 3. Results of resistance changes of PPy/PA composite film against temperature a) First heating; b) first cooling; c) second heating; d) second cooling

Conclusion

It seems that in the electrochemical preparation of conducting composite by making use of an IP and CP, the structure of IP plays an important role. The carbonyl-group moiety presence is essential, H-bonding does exist but these are not enough to explain the strong interaction between the two polymers. These interactions may well be a chemical bonding resulting in a graft copolymer, since the polymers behave quite different compare to the pristine conducting polymers. These are not the only spectroscopic and thermal differences but also the behavior towards electron donor/acceptor gases. The structures on the other hand have yet to be identified.

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