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OPTICAL PROPERTIES OF POLYANILINE SALT AND POLYANILINE BASE WITH KBr, $Co(CH_3COO)_2$ AND PICRIC ACID COMPOSITES

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Polyaniline was prepared by chemical methods. The composites were prepared by the hot pressing of polyaniline base with different percentages of KBr, $Co(CH_3COO)_2$ and picric acid. The diffused reflectance of polyaniline doped with 10, 15, 25 and 50 wt% of KBr, picric acid and cobalt acetate, was measured at room temperature in the wavelength range from 500 to 1800 nm. The energy gaps of the samples were then deduced as well as the position and number of the indirect transitions which were found to be dependent on the concentration percentage of the doping materials. The energy gaps of all samples decrease by increasing the concentration percentage of the doping materials.

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1. *Introduction*

Most organic compounds are known to be insulators. Metal – organic compound systems have been a subject of both theoretical and experimental interest because of their increasing technological importance. It is reasonable to expect significant changes in the electrical and optical properties when two polymers are blended together. The mixing of polymers has become commercially and technologically more important than the fabrication of homopolymers and copolymers in the last decade. Blending allows one to create new materials from the wide range of existing materials with specific properties for the desired application at low cost.

Among the conductive polymers, polyaniline (PANI) is of special interest. Aniline is a relatively inexpensive monomer. PANI can be easily synthesized with a good yield by polymerizing aniline in protonic acid aqueous solution in the presence of an oxidant [1–4], or electrochemically [5]. These advantages, coupled with its chemical stability and high conductivity in the doped state, make its commercial application quite attractive [6–9].

Polyanilines can be regarded as a conducting polymers [10] under certain stimulating conditions, like UV light, heat or addition of a suitable dopant to the polymer. Attempts have been made to improve the poor mechanical properties and the processibility of PANI by blending it with other polymers [11,12] or by substitution and copolymerization. Although blending of PANI with other polymers leads to a decrease of its conductivity, it is conceivable that composites with moderate conductivity and good mechanical properties can be obtained by the blending approach [13,14].

PANI was prepared by several methods [15,16]. The prepared PANI exists in four different forms, which was achieved through the protonation and doping of the base form. These forms have a wide range of electrical conductivity from insulating to conducting and optical [17].

In this study, preparation and optical absorbtion of PANI, PANI salt and of the composites prepared by hot pressing of PANI with KBr, $Co(CH_3COO)_2$ and picric acid have been investigated. This was to provide additional information about the nature and extent of intermoleclar interaction in such heterogeneous media.

By controlling the percentage of the dopant to PANI, it is possible to have a conducting polymers.

2. *Experimental*

Preparation of PANI. PANI is usually prepared by the redox polymerization of aniline using ammonium perdisulphate $(NH_4)_2S_2O_8$ as the oxidant. Distilled aniline (0.2M) was dissolved in 300 ml of precooled HCl (1.0M) solution and maintained at 0.5 °C. A calculated amount of ammonium perdisulphate (0.5M) dissolved in 200ml of HCl(1M), precooled to $0 - 5$ °C, was added to the above solution. The dark green precipitate resulting from this reaction was washed with HCl (1M) until the green colour disappeared. This precipitate was further extracted with tetrahydrofuran and dried to yield emeraldine salt. Emeraldine base can be obtained by heating the emeraldine salt with ammonia solution. The powder so obtained can be used for the device fabrication such as photovoltaics, photocells electrochronic and memory devices, battery electrode application, civil, military, photonic, optoelectronics and communications [15].

Samples of the emeraldine salt, emeraldine base and the composites prepared from the emeraldine base with different additives were pressed into pellets in a special vacuum mold. The pressure was 370 MPa (37 kN/cm^2). This pressure was sufficient to give compact specimens. After molding, the specimens were annealed at 1150 °C for 48 hours in a DC field of 90 V applied across the specimen. This thermal forming process was important to remove residual voids, improve the contact between the neighbouring particles and to orient the molecules with the axis of the specimen.

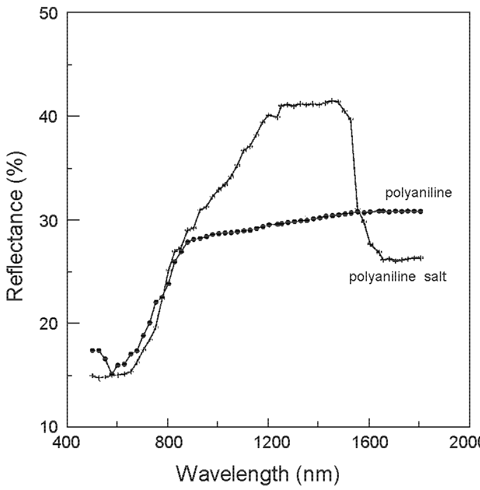
Optical measurements. The diffused reflectance measurements, in the range from 500 to 1800 nm, were carried out using the PMQ 111 spectrophotometer, which was fitted with an integrated-sphere diffuse reflectance attachment type RA3.

3. Results and discussion

Figure 1 shows the diffused reflectance spectra of PANI and PANI salt in the region 500 – 1800 nm at room temperature. From this figure, it is clear that for the PANI sample, the diffused reflectance increases with increasing wavelength to a maximum value of 1450 nm, decreases gradually as wavelength increases to 1600 nm and then remain constant. The diffused reflectance spectra of PANI salt show an increase of diffused reflectance with increasing wavelength and reach a maximum value at wavelength of 1000 nm and become constant with increasing wavelength. From this curve, one can see that there are two indirect optical transitions for PANI salt while there is one optical energy transition for PANI base.

Figure 2 shows the relation between the diffused reflectance and the wavelength for PANI with 10, 15, 25 and 50% KBr content. From this figure, it is clear that all samples have the same behaviour. The diffused reflectance increases sharply with increasing wavelength to a maximum value, then increases very slowly with increasing wavelength. From these curves, it is concluded that all these samples have one indirect optical transition and the optical transition decreases by increasing the KBr content.

Figure 3 shows the relation between the diffused reflectance and wavelength for polyaniline with 10, 15, 25 and 50wt% picric acid content. It can be seen that the



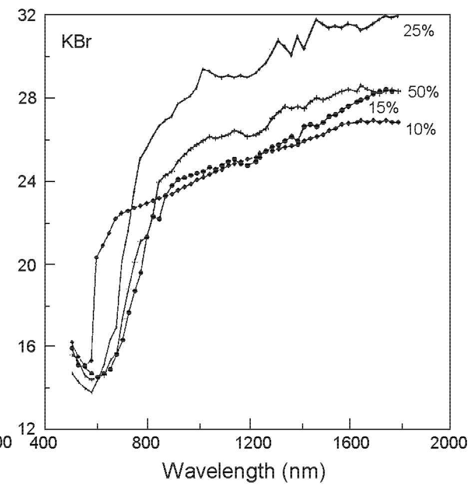
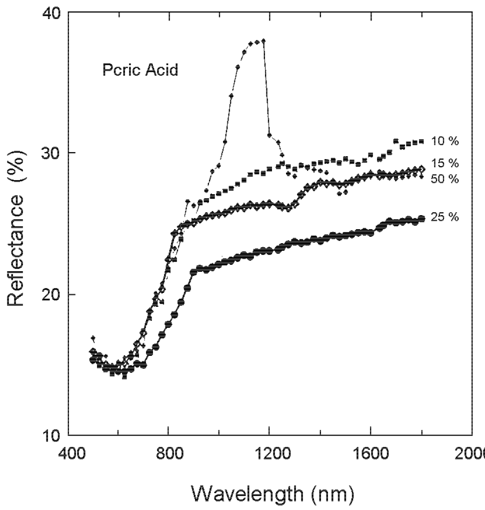


Fig. 1. Diffuse reflectance of polyaniline and polyaniline salt.

Fig. 2 (right). Diffuse reflectance of polyaniline with 10, 15, 25 and 50% KBr.

samples of polyaniline with 10, 15 and 25wt% picric acid content have the same behaviour. The diffused reflectance R increases strongly with the wavelength to a maximum value, then slowly increases with increasing wavelength, while in the case of the sample with 50wt% picric acid, the diffused reflectance increases to a maximum value at the wavelength of 1200 nm, then decreases with increasing λ to 1300 nm and after that it becomes nearly constant. This behaviour indicates that the samples with 10, 15 and 25wt% picric acid have one optical transition while the sample with 50wt% picric acid has two optical transitions. These optical transitions were found to decrease with increasing picric acid content.

Figure 4 shows the relation between the diffused reflectance R and the wavelength of PANI with 10, 15, 25 and 50wt% cobalt acetate content. From this figure, it is seen that these samples have the same behaviour. The diffused reflectance increases very sharply at low wavelength reaching a maximum value, and then increases very slowly with increasing wavelength. It is also clear that all these samples have one optical indirect transition which decreases with increasing the cobalt acetate content.



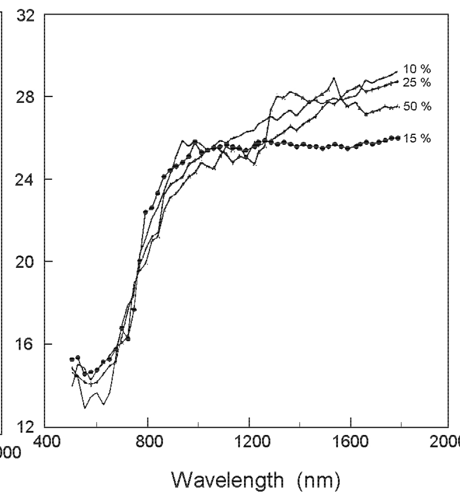


Fig. 3. Diffuse reflectance of polyaniline with 10, 15, 25 and 50% *picric acid.*

Fig. 4 (right). Diffuse reflectance of polyaniline with 10, 15, 25 and 50% *cobalt acetate.*

Figure 5 shows the relation between the energy gap and the concentration percentage of KBr, picric acid and cobalt acetate. It can be seen from this figure that all samples have one indirect optical energy gap except in the case of samples of PANI salt and PANI base with 50wt% picric acid which have two indirect optical energy gaps. It is found also that these energy gaps decrease sharply by increasing the concentration percentage of KBr, picric acid and cobalt acetate of 10wt% and 15 wt%, while for samples with 25wt% and 50wt%, the decrease is very slow.

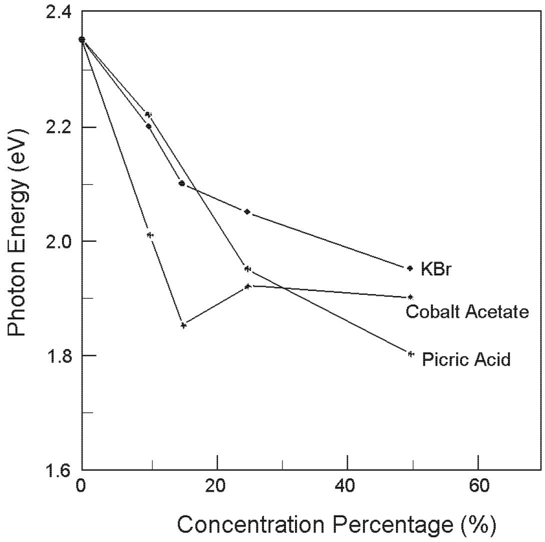


Fig. 5. Dependence of energy gap on concentration of additives in polyaniline.

It is also concluded from this figure that the PANI with 50wt% picric acid has the lowest energy gap. The decrease of the optical gap with increasing the concentration percentage of KBr, picric acid and cobalt acetate can be explained as follows. The addition of these materials to PANI increases the degree of disorder. The selective absorption of the photon energies of the incident light indicates that such energy is devoted to breaking up and hence deforming of partially crystalline structure of the polymers. Increasing the degree of disorder causes the band tail to increase [18], which, according to the electronic structure of amorphous materials, will lead to a decrease of the estimated optical gap.

4. Conclusion

PANI was prepared by chemical methods and the composites were prepared by hot pressing of PANI base with KBr, $Co(CH_3COO)_2$ and picric acid. The diffused reflectance of different samples of PANI with 10, 15, 25 and 50wt% of KBr, picric acid and cobalt acetate were measured at room temperature at wavelength from 500 up to 1800 nm. All samples have one indirect optical energy gap except in the case of PANI base with 50wt% picric acid and PANI salt which have two indirect optical energy gaps. The energy gaps of all these samples decrease by increasing the concentration percentage of KBr, picric acid and cobalt acetate. The decrease of the energy gap is due to the increase of the degree of disorder.

Thus, by controlling the concentration percentage of KBr, picric acid and cobalt acetate, it is possible to obtain the desirable properties. In this way, we obtain polymers with suitable energy gaps used for device fabrication such as photovoltaics and photocells.

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OPTIČKA SVOJSTVA SOLI POLIANILINA I BAZE POLIANILINA PUNJENOG S KBr, $Co(CH_3COO)_2$ I PIKRIČNOM KISELINOM

Polianilin smo pripremili kemijskim postupkom. Mješavine smo postigli vrućim tiskanjem polianilina s raznim postocima KBr, $Co(CH_3COO)_2$ i pikrične kiseline. Mjerili smo difuznu reflektanciju polianilina s 10, 15, 25 and 50 tež% KBr, pikrične kiseline i kobaltnog acetata na sobnoj temperaturi za valne duljine 500 do 1800 nm. Odredili smo energijske procjepe te položaje i broj posrednih prijelaza. Ustanovili smo za sve uzorke pad energijskih procjepa pri povećanju koncentracije dodataka.