

Synthesis and Study on Conductivity of Urethane Acrylate/Polyaniline/CuO Nanocomposites

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Abstract

In this research, novel conductive nanocomposites containing urethane acrylate (UA) and polyaniline/copper (II) oxide nanocomposites (PANi-CuO) were synthesized. At first polyaniline/CuO nanocomposites with different amount of CuO nanoparticles were prepared by chemical oxidation polymerization of aniline using ammonium peroxydisulfate as an oxidizing agent. Afterward, UA-PANi-CuO nanocomposites were mixed and then cured by ultraviolet irradiation. Analytical tests (FTIR and UV-vis spectroscopy, X-ray diffraction) approved chemical structure of synthesized materials. The SEM images of the nanocomposites showed uniform distribution of CuO nanoparticles in PANi matrix and UA-PANi-CuO in urethane acrylate matrix. Electrical conductivity measurements of PANi-CuO nanocomposites revealed that the conductivity of PANi decreased with adding content of CuO nanoparticles, also the conductivity of UA increased with adding PANi-CuO.

Keywords: *Polyaniline, CuO nanoparticles, UV cure, Urethane acrylate, Electrical conductivity.*

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Introduction

In recent years, conducting polymers with conjugated double bonds attracted attention as functional materials, due to their electrical, optical properties, low cost, high environmental stability and facility of processing, adaptability with flexible substrates and wide variety of applications in batteries, corrosion inhibition, super capacitors, microwave absorption, chemical sensor, separation membrane and electronic devices [1-6].

Among the conducting polymers, polyaniline has been extensively studied due to good environmental stability, facile synthesis, high conductivity, low cost, unique electrochemical, physicochemical properties and it shows sufficient stability for feasible applications [7-10].

Electrical conductivity of polyaniline in variety oxidation and protonation states is increasing by doping the base form of polyanilines with an acid to form a salt. There are three forms of PANi, namely, the fully reduced (leucoemeraldine), the fully oxidized (pernigraniline) state and the emeraldine base (half-oxidized). Among different forms of polyaniline, emeraldine is the most conductive form when in acidic solution doped to form green emeraldine salt [11]. Polyaniline synthesized from chemically or electrochemically methods that chemical method is very appropriate method for the mass production of PANi [12, 13].

The development of inorganic-organic nanocomposites have been receiving attention due to appropriate mechanical, electrical and optical properties and a wide range of potential applications in chemistry, medicine material science and biology. Polymeric nanocomposites were prepared from polymers and organic-inorganic materials at the nanometer scale, that were used in the different application such as microwave absorption layers, membranes, aerospace, coatings, adhesives, fire retardants materials, medical devices, gas sensors, super capacitors, etc [14-17].

Among of nanocomposites, PANi-inorganic nanocomposites were concerned because of their applications in many industrial fields. The nanocomposites of polyaniline can be synthesized by polymerization of aniline in the presence of dispersed inorganic nanoparticles. This polymerization can be done by three various methods. One of these methods is in situ chemical oxidation polymerization of aniline in an acidic solution with dispersion of inorganic nanoparticles in the presence of an oxidant at low temperature [18].

In recent years, nano scale metal oxides have attracted a great deal of research interest. Among all the metal oxides, cupric oxide (CuO) has attracted considerable attention due to wide applications in heterogeneous catalysts, gas sensors, solar cells, anticorrosion coatings, optoelectronic devices, catalysts, gas sensors, electrode materials, super conductors and so on [19, 20].

Solely polyaniline and its nanocomposites have disadvantages such as low mechanical properties that cause difficulty their use in industry. There are several ways to fix these problems, for example

mixing of polyaniline or its nanocomposites with other polymers such as epoxy resin or polyurethane to form a composition for casting or coatings.

Urethane acrylates (UA) are the most important UV curable oligomers that exhibit outstanding physical and mechanical properties such as toughness, flexibility, chemical resistance and environmental stability [21-23], so with the preparation of polyaniline and urethane acrylate composites can improve the mechanical properties of polyanilines.

In this research, UV curable nanocomposites containing urethane acrylate and PANi-CuO nanocomposite were prepared. This work has focused on the effect of PANi-CuO in urethane acrylate resin to prepare thin film UV curable conducting nanocomposite coating.

Experimental

Materials

Isophorone diisocyanate (IPDI), 2-hydroxyl ethyl methacrylate (HEMA), 1,6-hexanediol, dibutyltin dilaurate (DBTDL) as catalyst, aniline, ammonium peroxydisulfate (APS), hydrochloric acid, benzophenone and tripropylamine were purchased from Merck Company (Germany). Trimethylolpropane triacrylate (TMPTA) as reactive diluents were purchased from Aldrich Company (USA). Nano CuO (40 nm) was produced by US Research Nanomaterials Inc (USA).

Apparatus

FT-IR spectra of the PANi and PANi-CuO nanocomposites were recorded with Bruker Tensor 27 spectrometer in the region of 400-4000 cm^{-1} using KBr pellets. The optical absorption of nanocomposites in dimethyl sulfoxide (DMSO) solvent was measured at room temperature on UV-vis spectrophotometer in the range of 200-800 nm. XRD spectra of pure PANi and PANi-CuO nanocomposites were done at room temperature in the range from $2\theta=10-80^\circ$ on a Diano, using Cu $K\alpha$ radiation ($\lambda= 1.5406 \text{ \AA}$) at 40 kV and 30 mA. Electrical conductivity of pellets and films were measured with four point probe technique at room temperature. Pellets for measuring conductivity of the PANi and PANi-CuO nanocomposites were prepared by a compression-molding machine with hydraulic pressure (1 ton). The surface morphology of the products was carried out using scanning electron microscopy (LEO Company) operating at 10 kV.

Synthesis of PANi-CuO nanocomposites

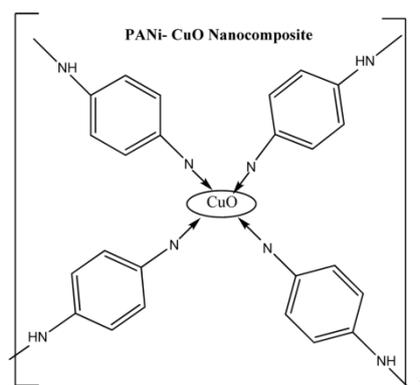
Polyaniline (PANi) was synthesized by oxidation polymerization in the presence of ammonium persulphate $[(\text{NH}_4)_2\text{S}_2\text{O}_8]$ as an oxidant according to the literature [21]. For preparing PANi-CuO nanocomposites, in a glass reactor which is placed in an ice bath, 0.24 mol fresh distilled aniline

and 25 ml of 0.1 mol hydrochloric acid solutions was added and stirred for half an hour. For preparing 1, 2.5 and 5% by weight PANi-CuO, 0.025, 0.05 and 0.1 g nano CuO for each sample was added in reactor, respectively (Table 1).

Table 1. Quantities of pure PANi and PANi-CuO (1-5 wt %) nanocomposites.

Sample	Aniline (g)	Nano CuO (g)	CuO in aniline (%)
PANi	2	0	0
PANi-CuO 1 wt%	2	0.025	1
PANi-CuO 2.5 wt%	2	0.05	2.5
PAN-CuO 5 wt%	2	0.1	5

Then 40 ml peroxydisulfate solution (1 molar) was added dropwise and kept stirred for 5 hours at 0 °C. Precipitated composition was filtrated and washed with hydrochloric acid solution and distilled water for several times and dried in a vacuum oven at 60 °C for 24 hours. The structure of PANi-CuO nanocomposite is presented in Scheme 1.



Scheme 1. Proposed structure of synthesized PANi-CuO hybrid nanocomposite.

Synthesis of urethane acrylate (PU) oligomer

Urethane acrylate oligomer was synthesized by two steps: at first step, 4.44 g isophorone diisocyanate (IPDI) and 1.18 g 1,6-hexanediol were mixed and then acetone (20 ml) as solvent and two drops of dibutyltindilaurate (DBTDL) as a catalyst were added and stirred at 45 °C for 2 hours. In the second step, 2.6 g hydroxyl ethylmethacrylate (HEMA) were added to reaction mixture and for 3 hours was stirred [24-26].

Synthesis of UA-PANi-CuO nanocomposites

Three different UA-PANi-CuO nanocomposites were prepared by adding and mixing of PANi-CuO nanocomposites (1, 2.5, 5 % CuO) into UA matrix. 10 g urethane acrylate and PANi-CuO nanocomposites (0.1, 0.25 and 0.5 g) were mixed and stirred for 1h. Finally, 0.33 g benzophenone (initiator) and 0.33 g tripropylamine (co-initiator) were added and mixed for 10 minutes. UA-PANi nanocomposite was synthesized in the same manner, but PANi was added into urethane acrylate. UA-PANi and UA-PANi-CuO nanocomposites films were prepared by using a film applicator on glass substrates with thickness about 120 microns. Then, films were cured by UV irradiation.

Result and discussion

Fourier transforms infrared (FTIR) analysis

PANi and PANi-CuO nanocomposites were characterized by using the FTIR technique. Figure 1 shows the FTIR pattern of PANi and PANi-CuO nanocomposites. FTIR spectrum of PANi (Figure-1a) shows all important absorption peaks at 3444, 2963, 2927, 1631, 1456, 1261, 1096 and 804 cm^{-1} . The peak at 3444 cm^{-1} is corresponding to N-H stretching. The bands at 2963 and 2927 cm^{-1} are due to aromatic C-H stretching vibrations. The bands at 1631 and 1456 cm^{-1} attributed to C=C stretching quinonoid and benzenoid rings of PANi, respectively. The peaks at 1261 and 1096 cm^{-1} are assigned to C-N stretching mode of benzenoid ring. The band at 804 cm^{-1} can be attributed to out-of-plane C-H bending.

The FTIR spectrum for PANi-CuO (5 %) nanocomposite shown in Figure-1b which shows some shift in the wavelengths and intensity of the peaks as compared to PANi, which indicates the structural change of polymer occurs when CuO nanoparticles were added to the PANi. The peak at 3432 cm^{-1} can be associated to the interaction between CuO nanoparticles and N-H group of PANi, so the peak displacement which was observed in FTIR spectrum may be ascribed to the formation of hydrogen bonding between CuO and the N-H group of PANi on the surface of the CuO nanoparticles [27].

The bands at 2962 and 2928 cm^{-1} were due to aromatic C-H stretching. The bands at 1597, 1427 cm^{-1} may be attributed to C=C stretching quinonoid and benzenoid rings of PANi, while bands at 1261 and 1099 cm^{-1} are assigned to C-N stretching mode of benzenoid units. The band at 802 cm^{-1} can be attributed to out-of-plane C-H bending.

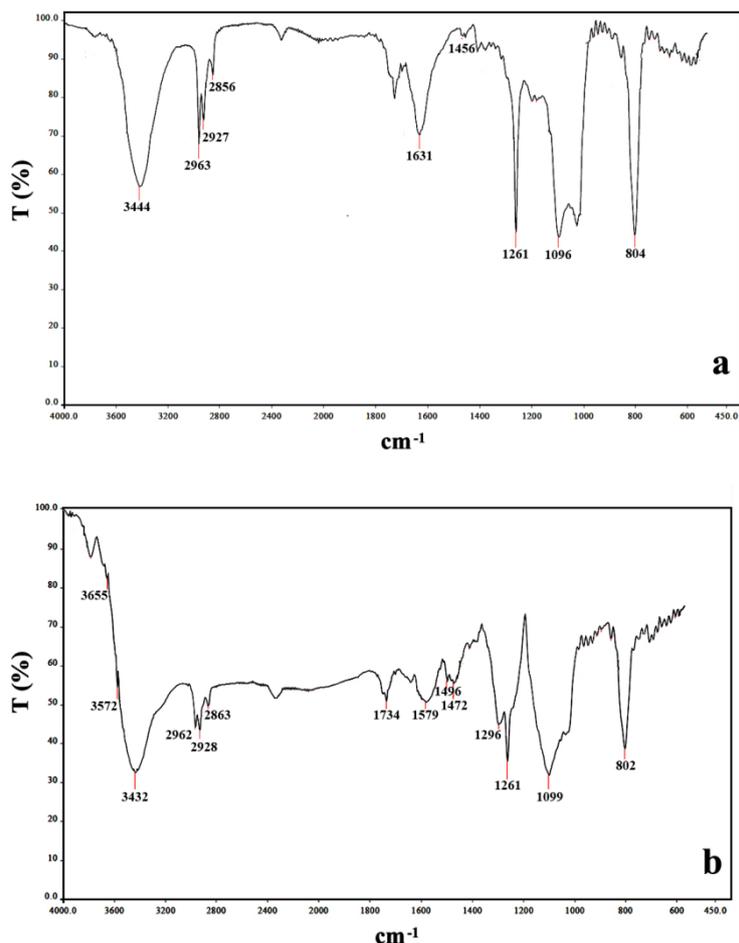


Figure 1. FTIR spectra of a) PANi (ES) and b) PANi-CuO (5 %) nanocomposites.

The FTIR spectrum for UA films is shown in Figure 2. The absorbance peak of -NCO group (2270 cm^{-1}) disappeared in FTIR spectrum. Figure 2 shows FTIR spectrum of UA in which the peak at 3417 cm^{-1} is corresponding to N-H stretching. The bands at 2961 and 2924 cm^{-1} are due to CH_2 and CH_3 groups, respectively. The bands at 1638 cm^{-1} attribute to C=O group and the peaks at 1261 cm^{-1} are assigned to C-N stretching mode.

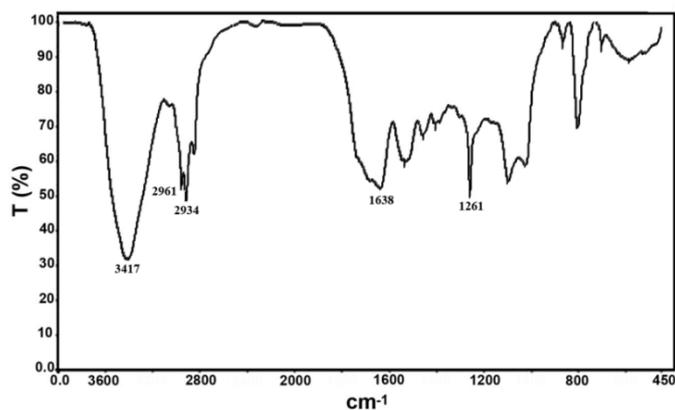


Figure 2. FTIR spectra UA film.

UV-vis spectroscopy analysis

The optical absorption spectrum is an important method to achieve optical energy band gap of crystalline and amorphous materials. The UV-visible absorption spectra of PANi (ES), PANi-CuO hybrid nanocomposites recorded at room temperature are given in Figure 3.

Figure 3a shows that two distinctive peaks of polyaniline appear at about 267 and 386 nm which are attributed to $\pi-\pi^*$ conjugated ring systems, and $\pi-\pi^*$ transition of the benzenoid ring. UV-visible spectra of nanocomposites were almost similar to those of PANi and some shifting in the bands was noticed. Figure 3b shows UV-visible spectrum of PANi-CuO (5 %) hybrid that shows two distinctive peaks at 271 and 390 nm [28, 29]. The red shift of the absorption transition to higher wavelength was due to the interaction of CuO nanoparticles with PANi matrix. Furthermore, by addition of CuO nanoparticles, intensities of the two absorption peaks decreased due to interaction between CuO nanoparticles with PANi.

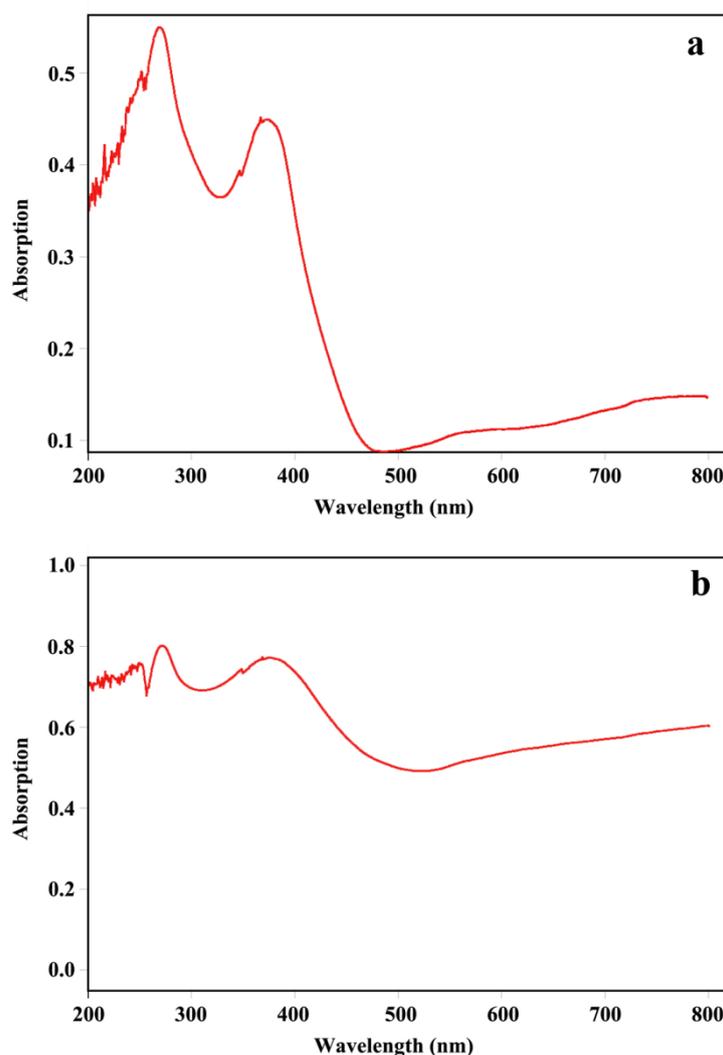


Figure 3. UV-vis spectra of a) PANi and b) PANi/ CuO (5 %) nanocomposite.

XRD analysis

XRD analysis was used to examine the structure of the PANi and PANi-CuO nanocomposites and investigate the effect of CuO nanoparticles on the PANi structure. Figure 4a shows the characteristic peaks of CuO nanoparticles at $2\theta = 32^\circ, 35^\circ, 39^\circ, 49^\circ, 53^\circ, 58^\circ, 62^\circ, 66^\circ, 68^\circ, 73^\circ,$ and 75° . Figure 4b shows the X-ray diffraction pattern of PANi amorphous nature in partially crystalline state with broad diffraction peaks of at about 25.5° [30]. XRD pattern of PANi-5% CuO nanocomposite (Figure 4e) shows two peaks of CuO nanoparticles at $2\theta = 35^\circ$ and 39° , XRD patterns of PANi-2.5 wt% and 1 wt% CuO composites show diffraction peaks almost similar to the free PANi (Figure 4c and 4d), due to low concentration of CuO did not significantly change in the structure of the PANi. These results confirmed the formation of PANi-CuO nanocomposites.

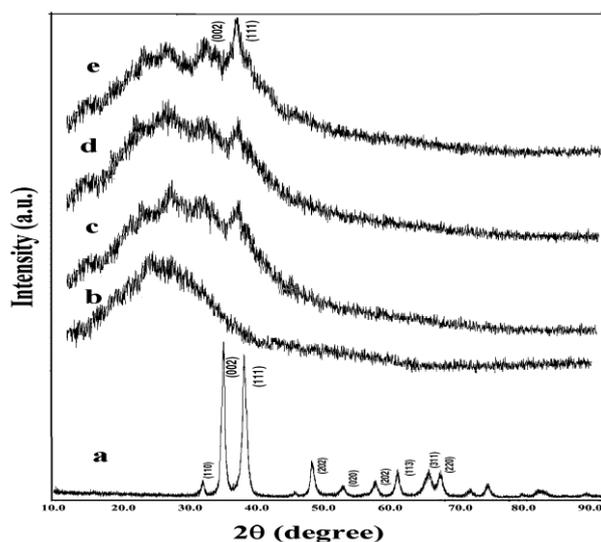


Figure 4. X-ray diffraction pattern of a) CuO nanoparticles, b) PANi (ES) and c-e) PANi-CuO (1, 2.5 and 5%) nanocomposites.

Morphologies

The morphologies of PANi (ES) and PANi-CuO (1-5 wt %) nanocomposites are shown in Figure 5. The SEM image of polyaniline shows clearly nano fibers structures with many pores and gaps among the fibers (Figure 5a₁) [31]. Figures 5a₂–a₄ showed SEM images of PANi-CuO hybrid nanocomposites (1-5%). According to the SEM images, PANi and CuO nanoparticles have formed a nanocomposite in which the nanoparticles are embedded in the polymer matrix.

SEM images showed that the loading of CuO nanoparticles have a powerful effect on the polyaniline's morphology and with the increase of the amount of CuO nanoparticles, a change in morphology of PANi is observed.

The morphologies of UA-PANi and UA-PANi-CuO nanocomposites films are shown in Figure 6. The SEM images showed that PANi-CuO nanocomposites have been distributed in the urethane acrylate matrix.

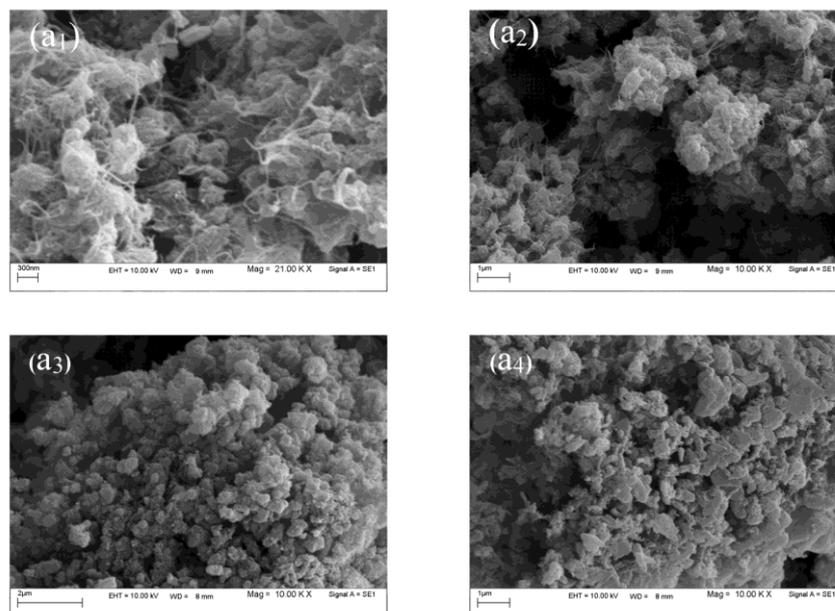


Figure 5. SEM images of a₁) PANi (ES), a₂-a₄) PANi-CuO (1, 2.5 and 5%) nanocomposites.

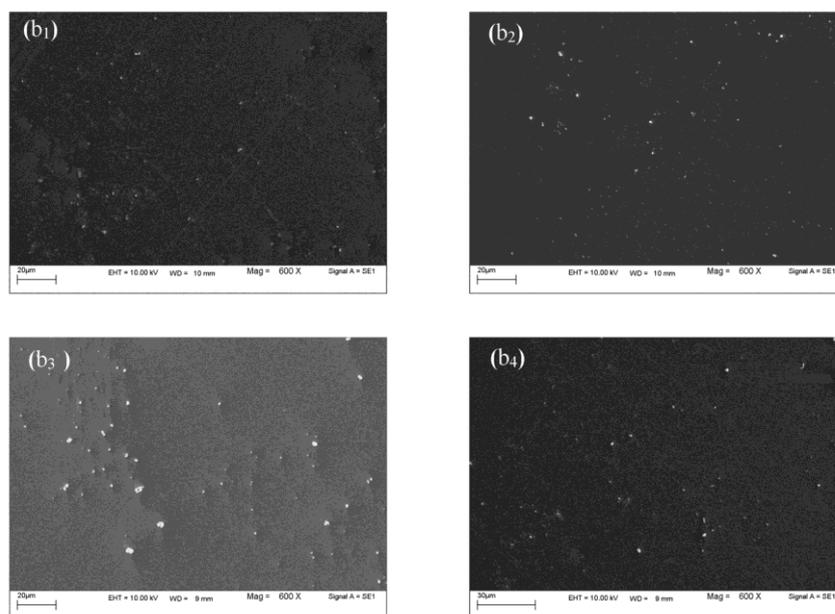


Figure 6. SEM images of b₁) UA-PANi (ES), b₂-b₄) UA-PANi-CuO (1, 2.5 and 5% CuO) nanocomposites films.

Electrical conductivity

Table 2 shows the variation of conductivity of pure PANi and PANi-CuO (1-5 wt % CuO) hybrid nanocomposites pellets. Electrical conductivity of PANi is $0.25 \Omega^{-1}\text{cm}^{-1}$ and the conductivity of

PANi is decreased with increasing of CuO nanoparticles in the PANi matrix. This can be attributed to adsorption of NH of PANi on the surface of CuO nanoparticles and bond formation in their structure. Also, the decrease conductivity of PANi-CuO nanocomposites may be ascribed to the behavior of CuO in the nanocomposites or reduction of doping degree. Additionally, increasing amount of CuO nanoparticles from 1 to 5 wt% influenced on electrical conductivity and decreased from 0.14 to $0.01\Omega^{-1}\text{cm}^{-1}$. The reason is that with increasing amount of CuO nanoparticles, bond formation between NH of PANi with CuO nanoparticles is increased and electrical conductivity of PANi-CuO nanocomposites is decreased [32].

Table 2. Conductivity of pure PANi and PANi-CuO (1-5 wt %) nanocomposites pellets.

Sample	Conductivity($\Omega^{-1}\text{cm}^{-1}$) at 300 K
Pure PANi	0.25
PANi-1 wt% CuO	0.14
PANi-2.5 wt% CuO	0.08
PANi-5 wt% CuO	0.01

Table 3 shows the variation of conductivity of pure UA, and UA-PANi-CuO (1-5 wt% CuO) hybrid nanocomposites films. The conductivity of the films increased with increasing PANi-CuO nanocomposites in the UA matrix. The conductivity depends on the nature of dopant, the inorganic nanoparticles concentration and the length of the conjugate chain, which have an important role in conductivity of the nanocomposites [32-35].

Table3. Conductivity of pure UA and UA-PANi-CuO (1-5 wt%) nanocomposites films.

Sample	CuO nano particles (wt %)	Conductivity($\Omega^{-1}\text{cm}^{-1}$) at 300 K
Pure UA	0	0.003
PU-PANi-CuO	1	0.015
PU- PANi-CuO	2.5	0.007
PU-PANI-CuO	5	0.005

Conclusion

UV curable novel conductive nanocomposites containing urethane acrylate and PANi-CuO nanocomposite were synthesized successfully. The structure of nanocomposite and interaction between PANi and CuO nanoparticles were confirmed by instrumental methods (FT-IR, UV-Vis and XRD studies). Also uniform distribution of CuO nanoparticles in PANi and PANi-CuO in UA-PANi-CuO nanocomposites were found by SEM images. Electrical conductivity measurements of PANi-CuO nanocomposites revealed that the conductivity of PANi decreased with adding content

of nano CuO, also the conductivity of UA increased with adding content of PANi-CuO nanocomposites.

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