

SURFACE MODIFICATION OF POLYMER NANOCOMPOSITES BY GLOW-DISCHARGE PLASMA TREATMENT

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A systematic study was carried out to characterize the effects of Argon-ion plasma on nanocomposite polymer membrane. Nanoparticles of cobalt (Co) are synthesized by the chemical route. Nanocomposite polymeric membranes 20 μm in size were prepared by using solution casting and spin coating method. The argon-ion plasma treatment was done for these membranes. The membranes were characterized prior to and after plasma treatment to perform the comparative study by using different techniques, such as the optical microscopy, scanning electron microscopy, and Fourier-transform infrared spectroscopy. The results show that the plasma treatment is a quite efficient tool for improving the surface and chemical properties of composite membranes with unique characteristics.

Keywords: polymer nanocomposites, synthetic membrane, plasma treatment, ion energy, plasma etching.

Metallic nanoparticles are traditionally synthesized by wet chemical synthesis. The chemicals used in this process are often toxic [1–3]. Since metal nanoparticles are widely used in biological applications [4], there is a growing need to develop environmentally friendly processes for nanoparticle synthesis that do not leave toxic byproducts [5–6]. The biological methods of nanoparticle synthesis using microorganisms, plants (including algae), fungi, bryophyte, pteridophyta, etc. were suggested as possible ecofriendly alternatives to chemical and physical methods [7–8]. Among various nanoparticles of transition metals, cobalt (Co) nanoparticles have recently received substantial attention for various reasons—like high refractive index [9], high electric conductivity [10], chemical catalysis [11] and antimicrobial activities [12].

Polymers became very important materials in modern manufacturing processes due to a great variety of chemical properties [13–14]. However, it is well known that permanent bonding [15], printing [16], coating [17], etc. are difficult for many polymers without surface pretreatment [18]. Therefore, the surface treatment of modified polymers has significant advantages in specific requirements to the surface properties, while the bulk properties remain unchanged [19–21]. The physical and chemical modifications of polymeric materials are also of great interest in artificial skin development and other biomedical applications [22].

The complex nature of plasma caused by the presence of ions, neutral particles, and radiation in discharge makes low-temperature plasmas widely applicable in the processes of fabrication of a growing number of materials, including etching of complex patterns and surface modifications of polymeric membranes [23]. The plas-

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ma surface treatment usually refers to plasma reactions that result either in a modification of the molecular structure of the surface or in the atomic substitution [24]. The accelerated electrons from the plasma have sufficient energy to induce cleavage of chemical bonds in the membrane structure and to form macromolecule radicals, which then initiate graft copolymerization [25]. Plasma treatment can be done either by regular plasma treatment or by plasma graft copolymerization (PGC) [26].

Various plasma components, such as electrons, ions, radicals, etc. are involved in this process. These components react on exposed surfaces. Since some parts of the surface are exposed to energies higher than the characteristic bond energy of polymers, these parts undergo scission reactions and form new bonding configurations on the surface [27]. The plasma treatment of polymer surface causes not only a modification during the plasma exposure but also leaves active sites on the surfaces subjected to the postreaction [28]. The glow-discharge plasma technique is especially useful for the functionalization of surfaces, as it is possible to modify the outermost surface layer by this technique [15, 29]. These factors improve the adhesion properties of the surface [30].

In the present work, we have synthesized polymer nanocomposites by using Co NPs and Polymethylmethacrylate (PMMA). These materials were exposed to Ar plasma and the variations of the surface and chemical properties were investigated.

Materials and Methods

In the present study, Co NPs were synthesized using *Mentha arvensis* (pudina) plant extract. The plant was washed with sterile distilled water. The plant extract was prepared by taking 25 g of thoroughly washed plant material in a 250 mliter Erlenmeyer flask with 100 mliter of distilled water and then boiling the mixture for 10 min in a water bath. The leaf broth was cooled and filtered through a Whatman No. 1 filter paper (with a pore size of 25 μm). For the preparation of Co nanoparticles, 10 mliter of the obtained plant extract were added to 90 mliter of 1 mM cobalt-nitrate solution and incubated in a rotary shaker for 2 h. The color of the solution changed from light yellow to brown indicating the formation of Co nanoparticles [31].

The Polymethylmethacrylate granules were obtained as a commercial grade from Loxim Polymers, Jaipur, and used to prepare flat sheet membranes by the solution cast method. The PMMA granules were weighed and dissolved in dichloromethane (CH_2Cl_2) to prepare a 10% solution. The solution was stirred by a magnetic stirrer to ensure the uniform dissolution and to enhance the rate of dissolution at room temperature for about 5 h. The 5% Co nanoparticles (of PMMA) were dispersed in a dichloromethane solvent using an ultrasonicator. This dispersed solution was added to the PMMA solution and stirred for about 30 min. The solution was put into flat-bottomed Petri dishes floating on mercury to ensure a uniform structure of the membranes. The solvent was allowed to slowly evaporate over a period of 10–12 h. The films obtained as a result were peeled off using forceps [32].

The plasma treatment device consisted of a source chamber with complete power supply connected to a vacuum system. A magnet is positioned to get a magnetic field (0.5 KG) inside the source chamber. Gaseous argon used to generate plasma was delivered into the source chamber by using a flow controller and applying the DC power between two electrodes. The confined plasma in the chamber was employed for surface modification. Applying a high voltage between two electrodes with magnetic field, we generated a DC glow discharge. The current in the upper and lower electrodes was maintained on a level of several mA and 3.2 KeV. In our study, we used Ar-plasma. This plasma was almost homogenous in a low-pressure glow discharge. The reaction chamber was evacuated and then refilled with low-pressure gaseous argon to create glow-discharge plasma. Plasma was energized by the direct current. The other energetic species in the plasma include radicals, electrons, and metastable photons in the short-wave UV range.

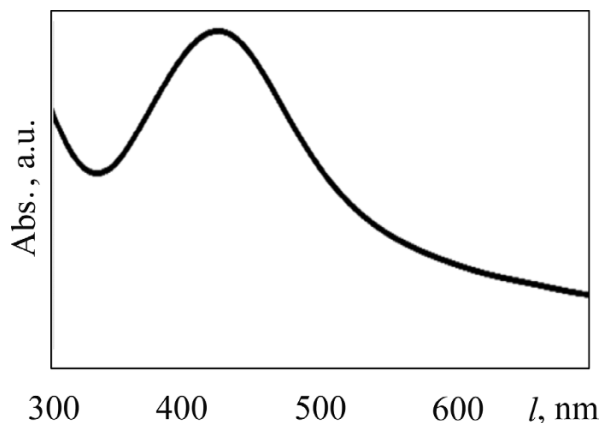


Fig. 1. UV-Vis absorption spectrum of Co NPs.

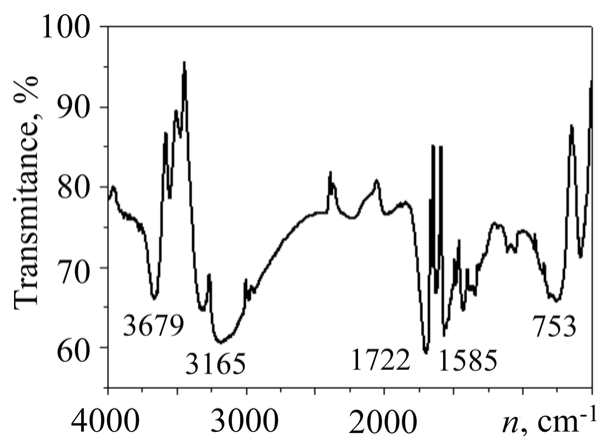


Fig. 2. FTIR spectra of vacuum-dried Co NPs.

The UV-Vis spectrum of NPs was taken using a SHIMADZU-1800 UV-Vis spectrophotometer. The FTIR analysis was performed in a FTIR spectrophotometer (IR Affinity-1 Shimadzu) within the range 4000–400 cm^{-1} to know whether possible functional groups are present with synthesized Co NPs. The scanning electron microscopic (SEM) analysis was realized using a scanning electron microscope (Carl ZEISS EVOR-18) operating at 20 kV. The morphology and particle sizes of Co NPs were also determined by the transmission electron microscopy (TEM) with a Technika TEM instrument operating at 200 kV.

Results and Discussion

The UV-Visible absorption spectrum shows the characteristic surface plasmon resonance (SPR) peak of Co NPs at 405 nm (Fig. 1) indicating the reduction of the cobalt-nitrate formation of Co nanoparticles. The absorption bands obtained using FTIR were classified as (A) stretching vibration of Co NPs at 763 cm^{-1} , (B) C=C unsaturated at 1285 cm^{-1} , (C) C=O stretching vibration at 1722 cm^{-1} , (D) CH_3 stretching vibration at 3166 cm^{-1} , and (E) C–H stretching vibration of aromatic compounds at 3679 cm^{-1} (Fig. 2).

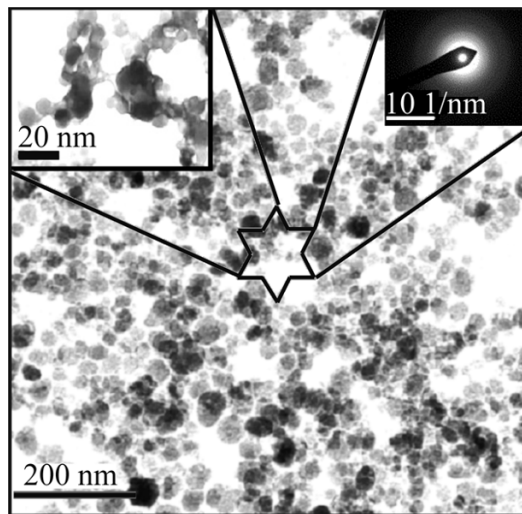


Fig. 3. TEM and diffraction pattern of Co NPs.

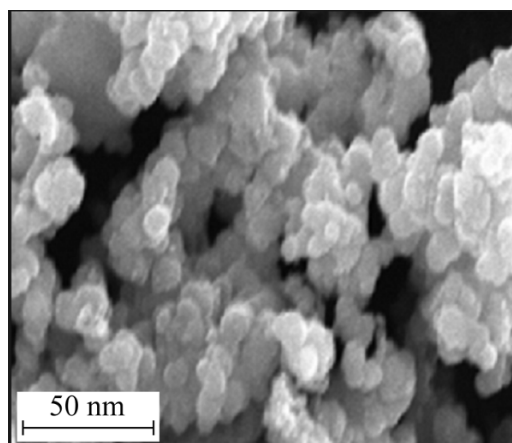


Fig. 4. SEM image of Co NPs: EHT = 10.0 kV; WD = 12.0 mm; signal A = SE1; Mag = 550.0 KX.

The Co NPs were dispersed in acetone by ultrasonication and used for the analysis of particle sizes (Fig. 3). The image clearly shows the spherical shape of NPs with particle sizes within the range 20–28 nm. The grain boundaries can be easily identified from the TEM images showing no aggregations in Co NPs. Here, for present study, the TEM image was the best indicator of the particle size. However, to determine the aggregation present in NPs for higher sample amounts, we have also recorded SEM images of the synthesized Co NPs (Fig. 4). The individual Co NPs can be easily identified in the image showing no aggregation in the NPs even for higher sample amounts. These Co NPs were used to synthesize Nanocomposite Polymer Membranes, plasma treatment was performed and characterized by using different techniques [15].

The FTIR spectra were obtained in the FTIR spectrometer. Fourier-transform infrared spectroscopy was used to gather information about the chemical structure of the compound and its chemical modification after plasma treatment. The FTIR images of the pristine and doped (untreated and plasma treated) membranes are shown in Fig. 5. Certain characteristic differences are detected at the peaks at certain wavelengths. These wavelengths served as indicators of changes in the chemical bonding and structure of the samples due to plasma treatment.

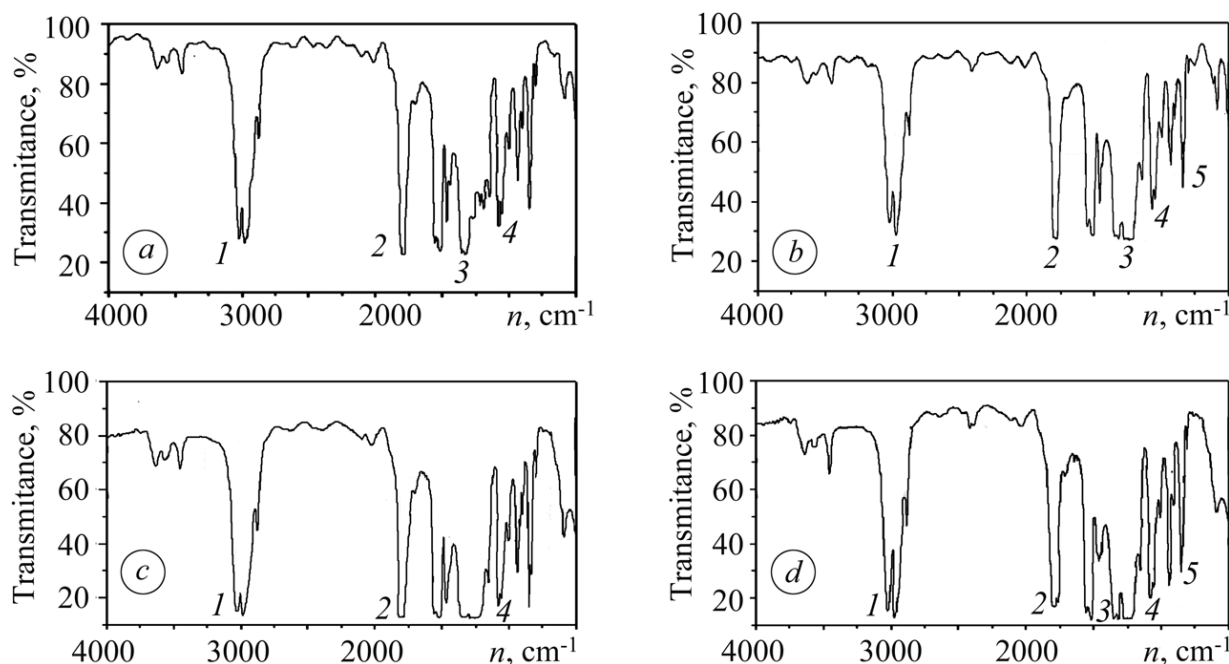


Fig. 5. FTIR spectra of pristine and Co nanocomposite polymer membranes both plasma treated and untreated: (a) pristine PMMA membrane; (b) Co nanocomposite PMMA membrane; (c) plasma treated pristine PMMA membrane; (d) plasma treated Co nanocomposite membrane [(1) 3100–2850 cm^{-1} characteristic of CH_3 ; (2) $\text{C}=\text{O}$ at 1770 cm^{-1} ; (3) 1125–1325 cm^{-1} characteristic of $\text{C}-\text{O}-\text{C}$; (4) $\text{C}-\text{O}$ at 1030 cm^{-1} ; (5) 765 cm^{-1} Co NPs characteristic].

The peaks at about 3000–2750 cm^{-1} were characteristic of the $-\text{CH}_3$ bonds. The similar peaks in the FTIR spectra of treated and untreated samples show that there are no changes in the basic structure of nanocomposite membranes. The increments in the absorption bands of $\text{C}-\text{O}$ at 1030 cm^{-1} and $\text{C}=\text{O}$ at 1770 cm^{-1} are attributed to the creation of unsaturated $-\text{C}=\text{C}-$ bonds at 1645 cm^{-1} after plasma treatment. It is also observed from the FTIR spectra that the $\text{C}-\text{C}$ and $\text{C}-\text{H}$ bands decrease after plasma treatment. This indicates that the cross-linking phenomenon is enhanced during plasma treatment. The Co NPs show their characteristic peak at 765 cm^{-1} for the nanocomposite membrane.

We study the surface morphologies of Co nanocomposite membrane by using SEM. The SEM images of the nanocomposite membrane are shown in Fig. 6. The scanning electron microscopic (SEM) analysis was performed by using the scanning electron microscope (Carl ZEISS EVOR-18) operating at 20 kV. The plasma treated nanocomposite membrane can be compared with the untreated membrane, which shows the improvement in porosity and roughness.

CONCLUSIONS

The color of solution changes from green to brownish as the plant extract is mixed in an aqueous solution of the cobalt ion complex, thus giving the primary indication of the formation of cobalt nanoparticles, which was further confirmed by analyzing these NPs by different techniques, such as the UV-Vis spectrophotometer, FTIR, TEM, and SEM.

The UV-Visible spectrum was obtained within a visible range 300–800 nm. A typical absorption peak of cobalt nanoparticles at 405 nm was obtained due to the surface plasmon vibrations of cobalt nanoparticles. The

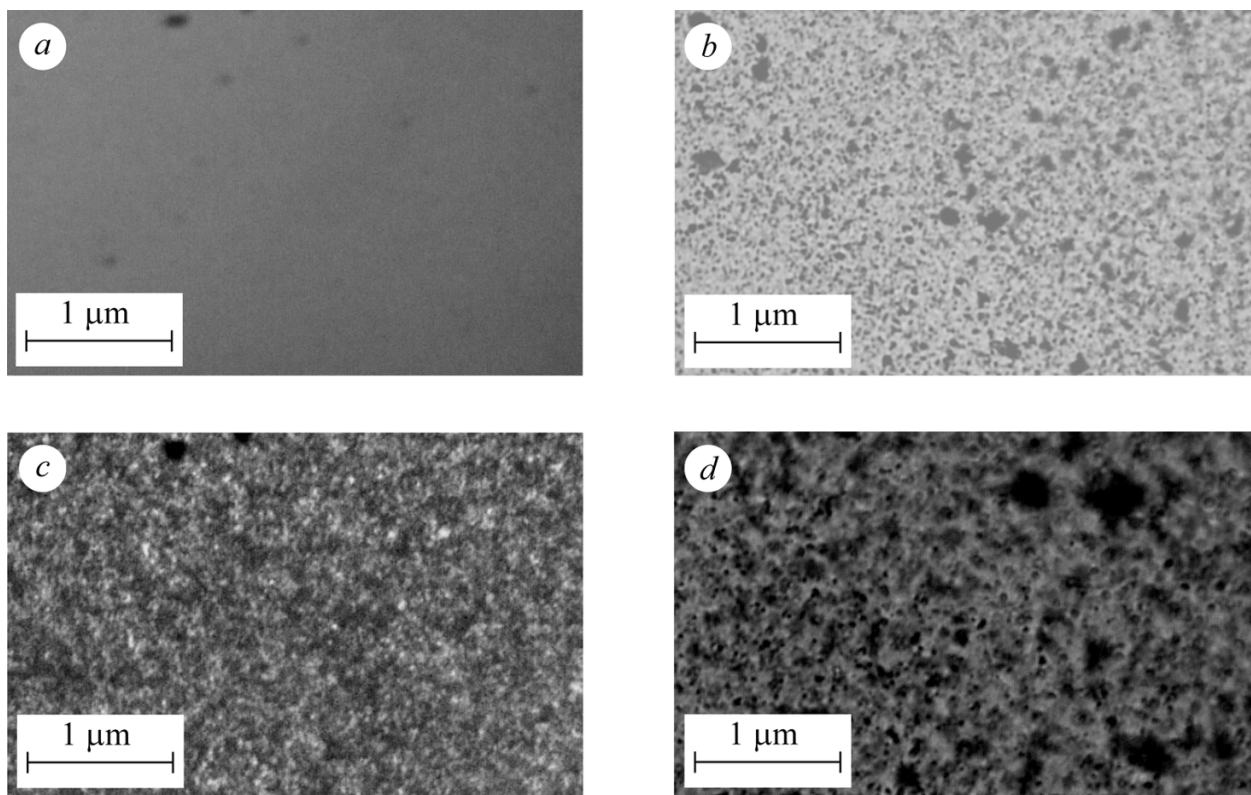


Fig. 6. SEM images of pristine and Co nanocomposite membrane both plasma treated and untreated (EHT = 10.0 kV; WD = 12.0 mm; Signal A = SE1; Mag = 150.0 KX): (a) pristine membrane; (b) 5% Co NPs Co nanocomposite membrane; (c) plasma treated pristine membrane; (d) plasma treated 5% Co nanocomposite membrane.

particle size of biosynthesized cobalt nanoparticles was further confirmed by the TEM and SEM measurements as equal to about 20–28 nm. The FTIR measurements were carried out to identify the possibility of interaction between the biomolecules and Co NPs. The FTIR measurements of biosynthesized cobalt nanoparticles showed the bands at about 763; 1605; 1722; 3165, and 3679 cm^{-1} .

The pristine PMMA membranes and the Co nanocomposite membrane (5 wt.%) were prepared by the solution cast method. The argon-plasma treatment technique applied in the present work showed a considerable improvement in the chemical and surface properties of the membranes. The plasma treatment helped in increasing the flux, whereas doping modified the surface properties. The SEM images showed high porosity and roughness after plasma treatment. As nanocomposite membranes were prepared without help of any support, it could be concluded that PMMA had a considerable strength as compared with the other polymeric materials, like polyamide, which could not be prepared without the help of support. The increments in the absorption bands of C–O at 1030 cm^{-1} and C=O at 1770 cm^{-1} are attributed to the creation of unsaturated –C=C– bonds at 1645 cm^{-1} after plasma treatment, while the decrease in the intensity of C–C and C–H bands indicates that the cross-linking phenomenon is enhanced after plasma treatment.

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