

SURFACE MODIFICATION OF POLYMER NANOCOMPOSITES BY GLOW DISCHARGE PLASMA TREATMENT

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Systematic study was carried out to characterize the effects of Argon ion plasma on nanocomposite polymer membrane. Nanoparticles of cobalt (Co) are synthesized by chemical root. 20 micron nanocomposite polymeric membranes were prepared using solution casting and spin coating method. Argon ion plasma treatment was done for these membranes. These membranes were characterized before and after plasma treatment to make comparative study by different technique such as optical microscopy, SEM-scanning electron microscope, Fourier transform infrared spectroscopy. Results show that plasma treatment is a quite effective tool for improving 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 where the chemicals used 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 the toxic by-products [5–6]. Biological methods of nanoparticle synthesis using micro-organisms, plants including algae, fungi, bryophyte, pteridophyta etc. have been suggested as possible ecofriendly alternatives to chemical and physical methods [7–8]. Among the various transition metal nanoparticles, cobalt (Co) nanoparticles have recently received substantial attention for various reasons – like high refractive index [9], high electrical conductivity [10], chemical catalysis [11] and antimicrobial activities [12].

Polymers have become very important materials in modern manufacturing processes due to a wide variety of chemical properties [13–14], but it is well known that permanent bonding [15], printing [16], coating [17], etc. are difficult on many polymers without surface pre-treatment [18]. Therefore, after-surface treatment of modified polymers has significant advantages in specific requirements of surface properties while retaining the bulk properties unchanged [19–21]. 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 due to presence of ions, neutrals and radiation in discharge makes low-temperature plasmas widely useable in a growing number of materials fabrication processes including etching of complex patterns and surface modifications of polymeric membranes [23]. Plasma surface treatment usually refers to plasma reaction that either results in modification of the molecular structure of the surface or atomic substitution [24]. The accelerated electrons from the plasma have suf-

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ficient energy to induce cleavage of the chemical bonds in membrane structure and to form macromolecule radicals, which subsequently initiate graft copolymerization [25]. Plasma treatment can be done by either regular plasma treatment, or plasma graft copolymerization (PGC) [26].

Various plasma components such as electrons, ions, radical 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]. Plasma treatment of polymer surface causes not only a modification during the plasma exposure, but also leaves active sites on the surfaces which are subjected to post-reaction [28]. Glow-discharge plasma technique is particularly useful for functionalization of surfaces as it is possible to modify outermost surface layer by this technique [15, 29]. These factors improve the adhesion properties of the surface [30].

In this paper we have synthesized polymer nanocomposites using Co NPs and Poly Methyl Meth Acrylate (PMMA). These materials were exposed to Ar plasma, and modification in the surface and chemical properties was 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 ml Erlenmeyer flask with 100 ml of distilled water, and then boiling the mixture for 10 min in a water bath. The leaf broth was cooled and filtered through Whatman No.1 filter paper (pore size 25 μm). For preparation of Co nanoparticles, 10 ml of the prepared plant extract was added to 90 ml 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].

PMMA granules were obtained as commercial grade from Loxim Polymers, Jaipur) and used to prepare flat sheet membranes by the solution cast method. 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 the solvent dichloromethane using 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 membranes. The Solvent was allowed to evaporate slowly over a period of 10...12 h. The films so obtained 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 K Gauss) inside the source chamber. Argon gas, used to generate plasma, was admitted into the source chamber using a flow controller and applying 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 generated the DC glow discharge. The current in the upper and lower electrodes was maintained at few mA and 3.2 KeV. In this study Arplasma was used. The plasma was almost homogenous in a low-pressure glow discharge. The reaction chamber was evacuated and then refilled with low-pressure Ar gas to create glow discharge plasma. Plasma was energized by direct current. Other energetic species in plasma include radicals, electrons and meta-stable photons in short-wave UV range.

UV-Vis spectrum of NPs was taken using UV-Vis spectrophotometer SHIMADZU 1800. FTIR Analysis was done using FTIR spectrophotometer (IR Affinity-1 Shimadzu) in the range of 4000...400 cm^{-1} for knowing the possible functional groups present with synthesized Co NPs. Scanning Electron Microscopic (SEM) analysis was done using Scanning electron microscope (Carl ZEISS EVOR-18) operated at 20 kV.

Morphology and particle size of Co NPs were also determined using transmission electron microscopy (TEM) Technika TEM instrument operating at 200 kV.

Results and discussion. UV-Visible absorption spectrum shows the characteristic surface plasmon resonance (SPR) peak of Co NPs at 405 nm (Fig. 1), indicating reduction of cobalt nitrate formation of Co nanoparticles. 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 3679 cm^{-1} of aromatic compounds (Fig. 2).

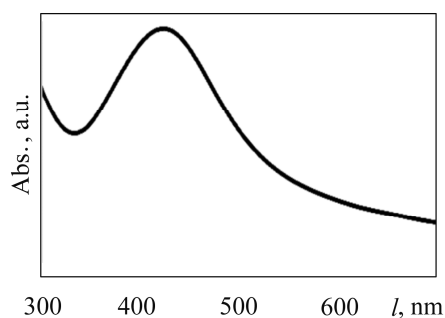


Fig. 1.

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

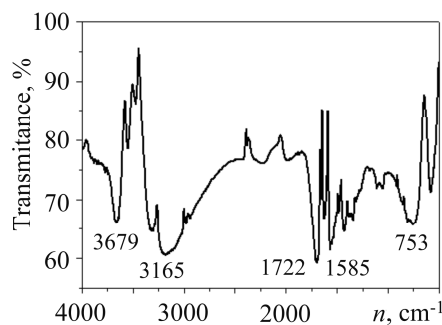


Fig. 2.

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

Co NPs were dispersed in acetone by ultra-sonication and used for particle size analysis (Fig. 3). Image clearly shows the spherical shape NPs with particle size ranging from 20...28 nm. Grain boundaries can be easily identified from TEM images showing no aggregations in Co NPs. Here for present study, TEM image was the best indicator of the particle size. But to determine aggregation present in NPs at higher sample amounts, we have also recorded SEM images of the synthesized Co NPs (Fig. 4). As individual Co NPs can easily be identified from the image, showing no aggregation in NPs even at higher sample amount. These Co NPs were used for synthesis of Nanocomposite Polymer Membranes, plasma treatment was done and characterized using different techniques [15].

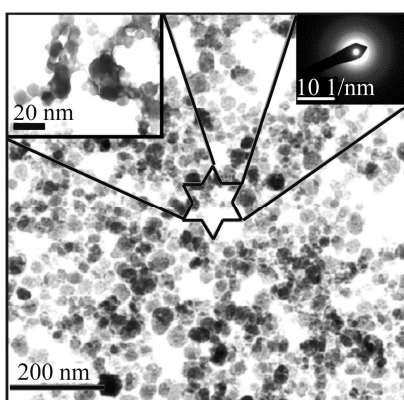


Fig. 3.

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

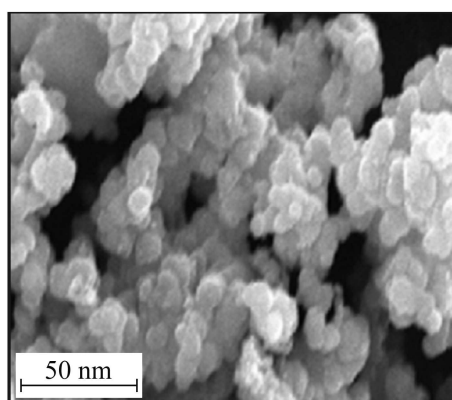


Fig. 4.

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

FTIR spectra were obtained on FTIR spectrometer. FTIR was used to gather information about the chemical structure of a compound and chemical modification after plasma treatment. The FTIR images of the pristine and doped (untreated and plasma treated) membranes are as shown in Fig. 5. Certain characteristic differences are noticed at the peaks at certain wavelengths. These wavelengths were indicators of the change in the chemical bonding and structure of the samples due to plasma treatment.

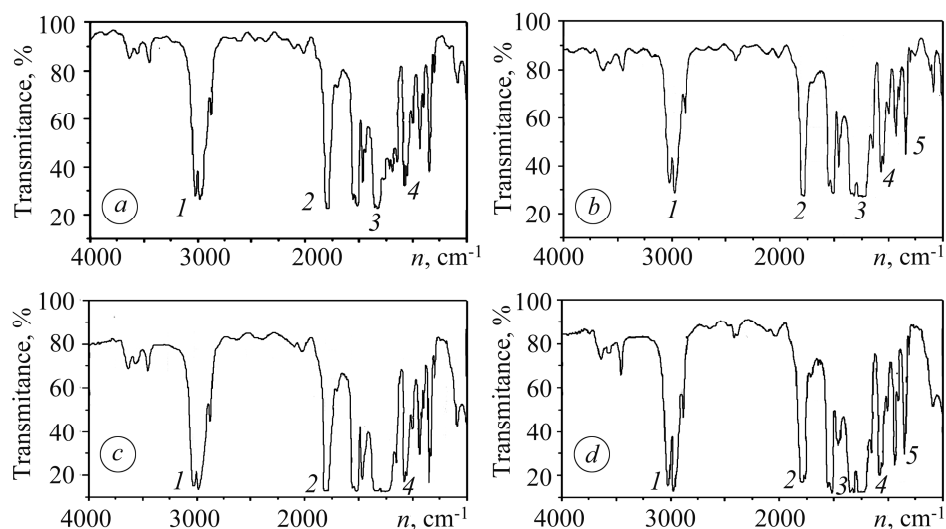


Fig. 5. FTIR spectra of pristine and Co nanocomposite polymer membrane both plasma treated and untreated: *a* – pristine PMMA membrane; *b* – Co nanocomposite PMMA membrane; *c* – plasma treated pristine PMMA membrane; *d* – plasma treated Co nanocomposite membrane. (1 – 3100...2850 cm^{-1} characteristic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

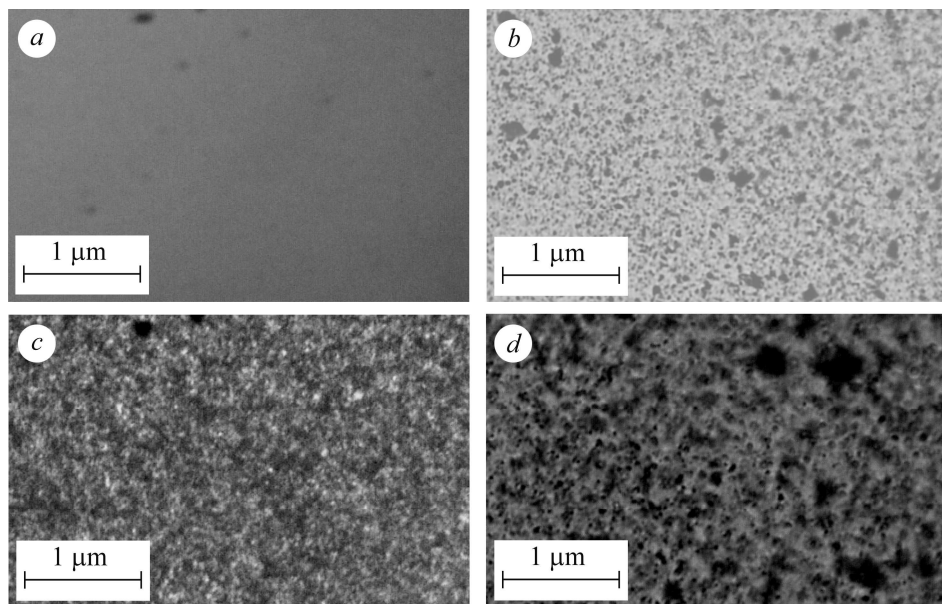


Fig. 6. SEM images of pristine and Co nanocomposite membrane both plasma treated and untreated (EHT = 10.0 kV; WD = 12.0 mm; Signal A = SE1; Mag = 150.0 KX): *a* – pristine membrane; *b* – 5% Co NPs Co nanocomposite membrane; *c* – plasma treated pristine membrane; *d* – plasma treated 5% Co nanocomposite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

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

We investigated surface morphologies of Co nanocomposite membrane using SEM. The SEM images of nanocomposite membrane are shown in Fig. 6. Scanning Electron Microscopic (SEM) analysis was done using Scanning electron microscope (Carl ZEISS EVOR-18) operated at 20 kV. Plasma treated nanocomposite membrane can be compared with untreated one which shows the improvement in porosity and roughness.

CONCLUSIONS

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

The UV-Visible spectrum was obtained in a visible range of 300 to 800 nm. A typical absorbance peak at 405 nm of cobalt nanoparticles was obtained due to the surface Plasmon vibrations of cobalt nanoparticles. Particle size of biosynthesized cobalt nanoparticles was further confirmed by TEM and SEM measurements which were about 20...28 nm. The FTIR measurement was carried out to identify the possible interaction between biomolecule and CoNPs. The FTIR measurements of biosynthesized cobalt nanoparticles showed the bands of about 763; 1605; 1722; 3165 and 3679 cm^{-1} .

The pristine PMMA membranes and Co nanocomposite membrane (5 weight%) were prepared by the solution cast method. The Ar plasma treatment technique applied here showed considerable improvement in the chemical and surface properties of membranes. 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 considerable strength as compared to 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} were attributed to the creation of unsaturated $-\text{C}=\text{C}-$ bonds at 1645 cm^{-1} after plasma treatment, while decrease in intensity of C–C and C–H bands indicated that cross linking phenomenon enhanced after plasma treatment.

РЕЗЮМЕ. Досліджено вплив іонно-плазмової обробки на властивості мембрани з нанокompозитного полімеру. Наночастинки кобальту одержано хімічним синтезом. Мембрани завтовшки 20 μm виготовлено нанесенням нанокompозитного полімеру з розчину з подальшою іонно-плазмовою обробкою. Мембрани вивчено перед та після їх обробки плазмою методами оптичної мікроскопії, сканівної електронної мікроскопії та інфрачервоної Фур'є-спектроскопії. Виявлено, що іонно-плазмова обробка – ефективний засіб поліпшення поверхневих та хімічних властивостей мембран з нанокompозитних матеріалів.

РЕЗЮМЕ. Исследовано влияние ионно-плазменной обработки на свойства мембраны из нанокompозитного полимера. Наночастицы кобальта получены химическим синтезом. Мембраны толщиной 20 μm изготовлены нанесением нанокompозитного полимера с раствора с последующей ионно-плазменной обработкой. Мембраны изучены до и после обработки плазмой методами оптической микроскопии, сканирующей электронной микроскопии и инфракрасной Фурье-спектроскопии. Вывявлено, что ионно-плазменная обра-

ботка – эффективное средство улучшения поверхностных и химических свойств мембран с нанокompозитных материалов.

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