

Surface Modification of Polymer Nano Composites by Glow Discharge Plasma Treatment

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ABSTRACT

Systematic study was carried out to characterize the effects of Argon ion plasma on nano composite polymer membrane. Nano particles of Cobalt (Co) are synthesized by chemical route. 20 micron nano composite 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 Nano Composites, Synthetic Membrane, Plasma Treatment, Ion Energy, Plasma Etching.

INTRODUCTION

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]. So, there is a growing need to develop environmentally friendly processes for nanoparticle synthesis that do not left 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 wide varieties 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 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 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 molecular structure of the surface or atomic substitution [24]. The accelerated electrons from the plasma have sufficient 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 or 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 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 with Ar plasma, and modification in 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 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 1mM 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 solution cast method. PMMA granules are weighed and dissolved in dichloromethane (CH₂Cl₂) to prepare a 10% solution. The solution is stirred by magnetic stirrer to ensure the uniform dissolution and to enhance the rate of dissolution at room temperature for around 5 hours. 5 % Co nanoparticles (of PMMA) were dispersed in the solvent dichloromethane using ultra-sonicator. This dispersed solution was added to the PMMA solution and stirred for around 30 minutes. The solution was put into flat-bottomed petri-dishes floating on mercury to ensure a uniform structure of membranes. Solvent was allowed to evaporate slowly over a period of 10-12 hours. The films so obtained were peeled off using forceps [32].

Plasma treatment consists 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 for generate plasma is admitted into source chamber using a flow controller and applying DC power between two electrodes. The confined plasma in the chamber is used for surface modification. Applying a high voltage between two electrodes with magnetic field generates the DC glow discharge. The current in the upper and lower electrodes is maintained at few mA and 3.2 KeV.

In this study we have used Ar plasma. The plasma is almost homogenous in a low-pressure glow discharge. The reaction chamber is evacuated and then refilled with low-pressure Ar gas to create glow discharge plasma. Plasma is 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 20kV. Morphology and particle size of Co NPs are also determined using transmission electron microscopy (TEM) Technika TEM instrument operating at 200 kV.

RESULTS AND DISCUSSION

UV-Visible absorption spectrum shows characteristic surface plasmon resonance (SPR) peak of Co NPs at 405 nm (Figure 1), indicating reduction of cobalt nitrate formation of Co nanoparticles. Absorption bands obtained using FTIR are 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 (Figure 2).

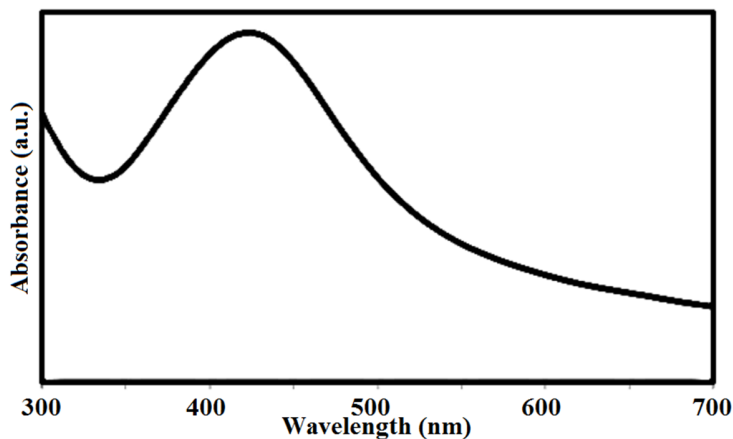


Fig 1. UV-Vis absorption spectrum of Co NPs.

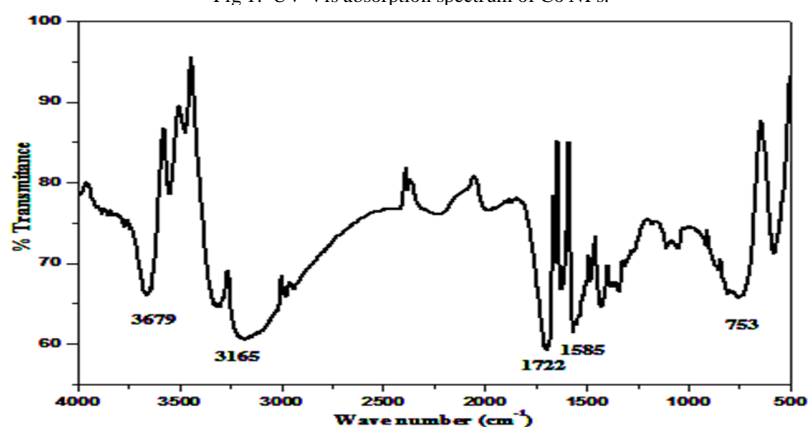


Figure 2. FTIR spectra of vacuum dried Co NPs.

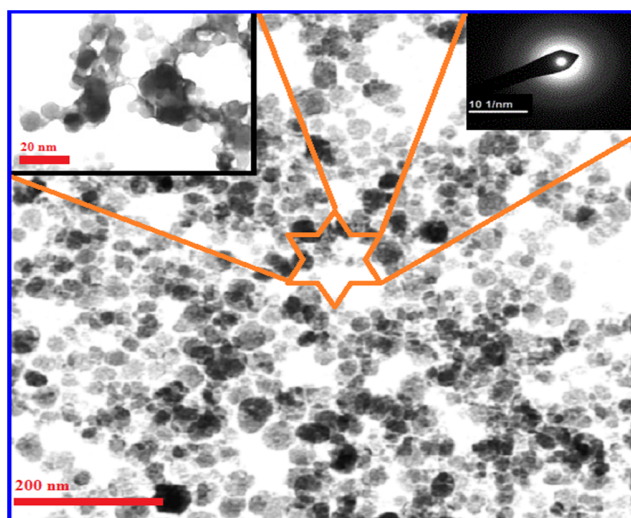


Figure 3. TEM & diffraction pattern of Co NPs.

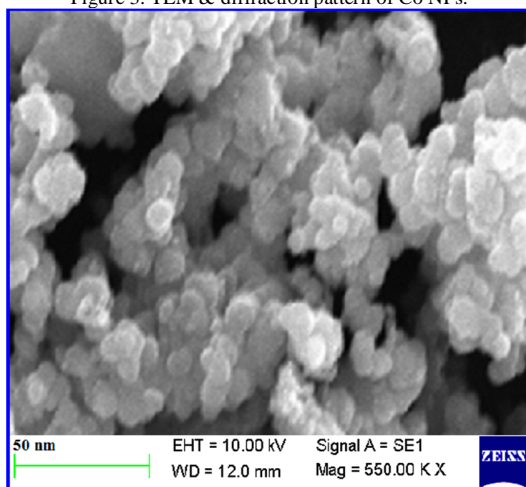


Figure 4. SEM image of Co NPs.

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

FTIR spectra are obtained on FTIR spectrometer. FTIR is 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 the Figure 5. We notice certain characteristic differences in peaks at certain wavelengths. These wavelengths are indicators of change in the chemical bonding and structure of the samples due to plasma treatment.

The peaks at around $3000\text{-}2750\text{ cm}^{-1}$ are characteristic of -CH_3 bonds. The similar peaks in the FTIR spectra of treated and untreated samples show that there is 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} has been attributed to the creation of unsaturated -C=C- bonds at 1645 cm^{-1} after plasma treatment. It is also observed from FTIR spectra that C-C and C-H bands have been decreased after plasma treatment. It indicates that cross linking phenomenon enhanced during plasma treatment. While Co NPs are showing its characteristic peak in 765 cm^{-1} for nano composite membrane.

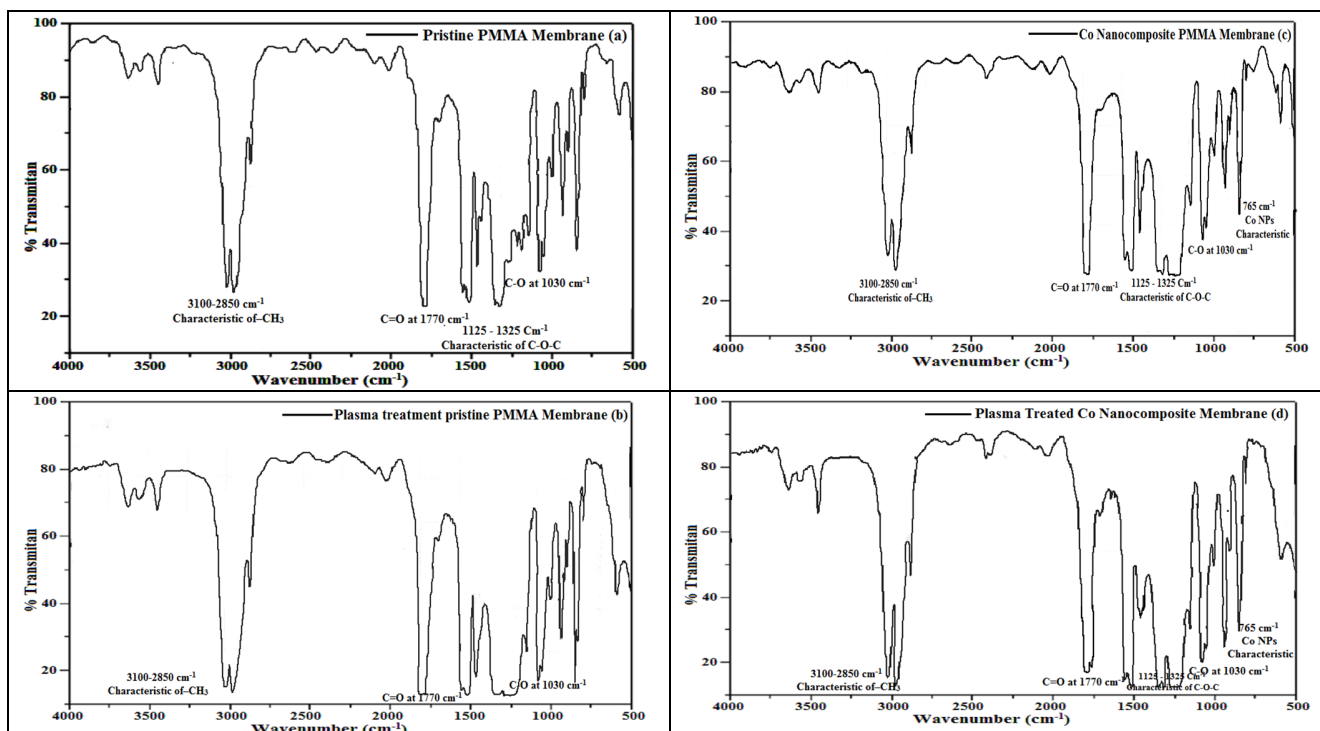
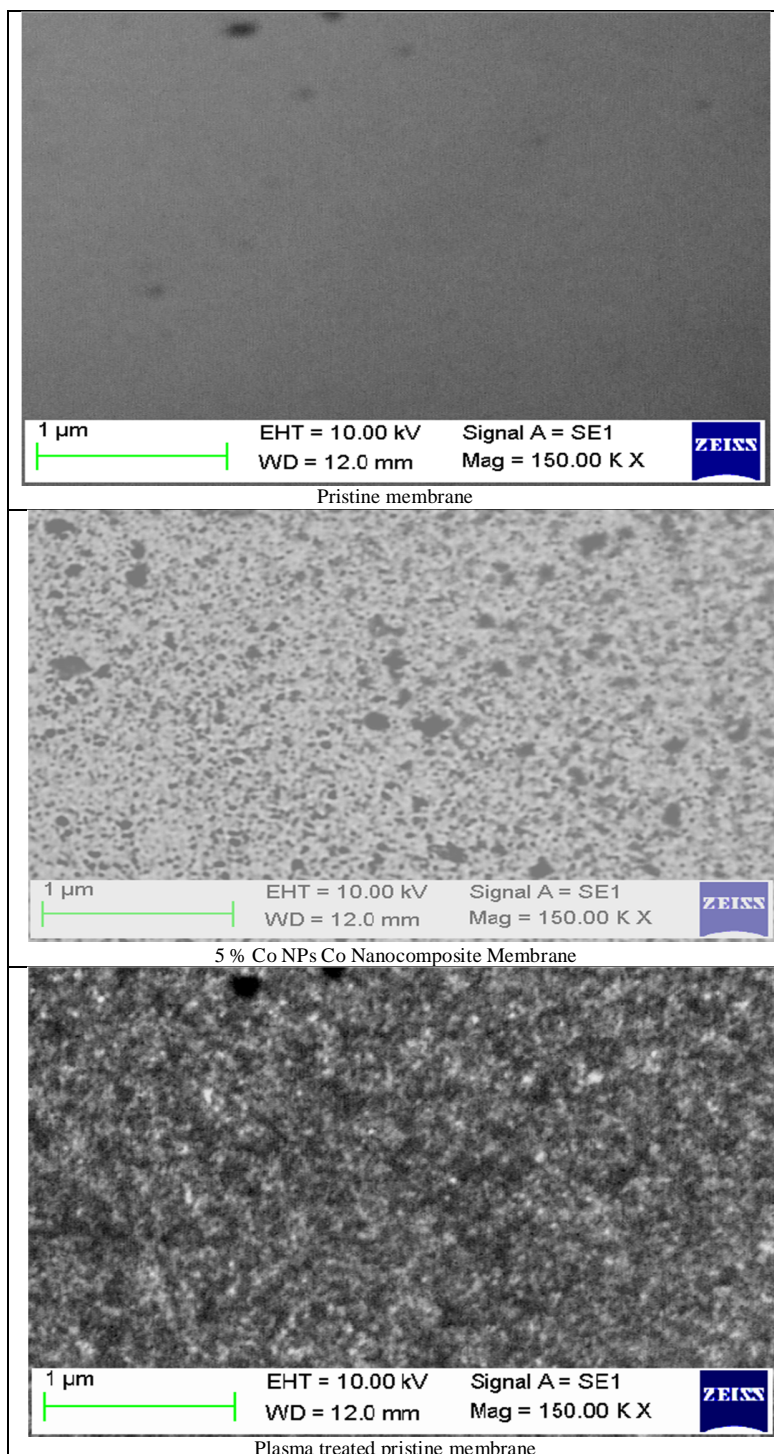


Figure 5. FTIR spectra of pristine and Co Nanocomposite Membrane both plasma treated and untreated.

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



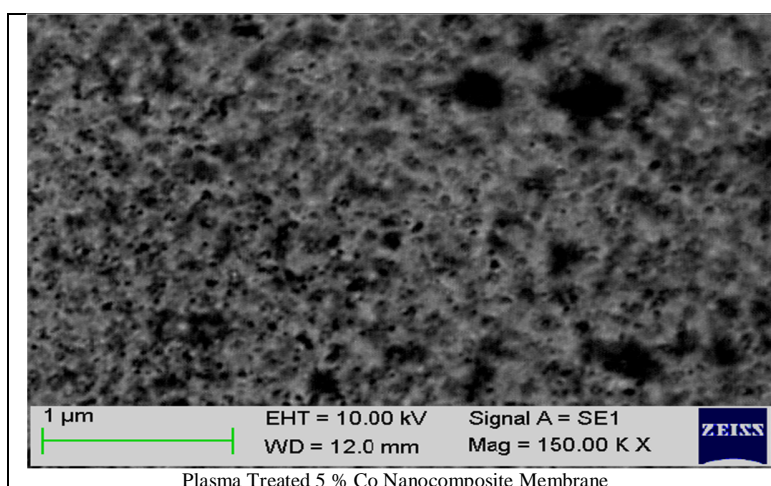


Figure 6. SEM images of pristine and Co Nanocomposite Membrane both plasma treated and untreated.

CONCLUSIONS

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

UV-Visible spectrum obtained in visible range of 300nm to 800nm. 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 were further confirmed by TEM and SEM measurements which comes around 20- 28 nm. FTIR measurement carried out to identify the possible interaction between biomolecule and Co NPs. The FTIR measurements of biosynthesized cobalt nanoparticles show bands at around 763, 1605, 1722, 3165 and 3679 cm^{-1} .

Pristine PMMA membranes and Co nanocomposite membrane (5 weight %) were prepared by solution cast method. Ar Plasma treatment technique applied here has shown considerable improvement in chemical and surface properties of membranes. Plasma treatment has helped in increasing flux whereas doping has modified the surface properties. SEM images show high porosity and roughness after plasma treatment. As nanocomposite membranes are prepared without help of any support, it can be concluded that PMMA has considerable strength as compared to other polymeric materials like polyamide which cannot 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} has been attributed to the creation of unsaturated –C=C– bonds at 1645 cm^{-1} after plasma treatment, While decrease in intensity of C-C and C-H bands indicates that cross linking phenomenon enhanced after during plasma treatment.

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