Fabrication of biocompatible nanocomposite consisted of zinc oxide nanoparticles based poly (Acrylonitrile-co-Acrylic acid)

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Abstract

The addition of appropriate additives can change the properties of the polymer matrix. Nanocomposites are useful because of its high aspect ratio. Selection of additives which can make a cheaper and multifunctional material is one of the major issues. ZnO nanoparticles can be used as an additive in preparing biocompatible and biodegradable nanocomposite which would have several analytical and biomedical applications. ZnO nanoparticles are multifunctional materials and in recent years they drawn an increasing attention because of its physical and chemical stability, high catalysis activity, effective antibacterial and bactericide function and intensive UV and IR absorption. Hence considering the above reasons, in the present study the incorporation of different amounts of ZnO powder inside the P oly(acrylonitrile-co-acrylic acid) is done by a low cost physico-mechanical method to prepare polymer nanocomposite for multiple purposes. The as synthesized ZnO based Poly(acrylonitrile-co-acrylic acid) composite sheets were characterized by various analytical techniques such as FTIR, Raman Spectroscopy, SEM, XRD and TGDTA. The analyses indicated the uniform dispersion of ZnO nanoparticles inside the polymer matrix resulted in crystalline structure which resulted in improved thermal stability and low water holding capacity and swelling ratio. The as synthesized nanocomposites were effectively utilized for biological activities. Copyright © 2018 VBRI Press.

Keywords: Nanocomposite, ZnO nanoparticles, polymer; characterization, application.

Introduction

The polymer composites are the substances which are formed by the combination of two or more substances that are chemically and physically different and separated by a distinct interface. The composite achieved is of good use and have better properties which can't be achieved by any of the constituent alone [1]. The fillers added to the polymer matrix may be organic, inorganic and metal particles. The inorganic filled polymer composites are much better and have many benefits because they are easily processed, have low cost and good performance over the metals. [2]. Polymer composites also have many applications in industrial side because of its properties that is polymer composites are hard, having low density, high melting point, thermal conductivity and chemical stability. Their mechanical properties also become improved which make them applicable in many applications. [3,4]. Because of the excellent properties of the polymer composites like greater hardness, elevated melting point, high thermal conductivity, less density, decreased coefficient of thermal expansion, and improved mechanical properties they have good potential for various industrial fields.[3].

ZnO is a multifunctional nanoparticle and in recent years it has drawn an increasing attention because it is both physically and chemically stable, can be used in catalytic activity, also it is effective against antibacterial and bactericide function and is capable of UV and IR adsorption [5].

Several studies involving ZnO as an additive in making polymeric composites have been reported to achieve various applications. zinc oxide based acrylonitrile-butadiene-styrene composites for studying the tribological behavior of the polymer composite [2]. ZnO nanoparticles and its composites with different molar concentration of polyaniline (PANI) have been reported. The results showed that properties of PANI were changed due to interaction of zinc oxide nanoparticles with the polymer matrix [6,7,8].

Various ZnO based polyvinyl alcohol (PVA) composites are reported for getting good physical properties and their antimicrobial and other applications. [3,9,10]. Guo et al [11] prepared the Fe_3O_4 based poly (acrylonitrile-co-acrylic acid) nano composites with

magnetic behavior using electrospinning process. Chae et al [12] synthesized the polyacrylonitrile (PAN) and ZnO nanocomposites by solution mixing and film casting method. The results showed that the internalization of ZnO developed the ability of PAN to be thermally stable at very less amount of ZnO. Sebastian et al [13] prepared 1%, 2% and 4% ZnO based ethylene vinyl acetate nanocomposites using sonicator method. For the determination of the thermal stability TGA-DTA analysis was carried out showing that increasing zinc oxide amount gradually increases the thermal stability of the polymer composites. Korobeinyk et al [14] reported that the doping of PAN changed its physicochemical properties and enhanced its thermal stability.

Polymers are usually insulators and have limited applications in electroanalytical and biomedical fields. The addition of appropriate additives can change the properties of the polymer matrix. Selection of appropriate additives which can make a cheaper and multifunctional material is one of the major issues. ZnO nanoparticles based composite is one of the multifunctional nanocomposites. Hence keeping in view the above mentioned points, the incorporation of ZnO nanoparticles powder inside the Poly(AN-co-AA) is done to prepare a polymer composite by a low cost physico-mechanical method to obtain nanocomposites with improved properties for multiple applications.

Experimental

Chemicals and reagents

Zinc oxide (ZnO) nano powder was obtained from Sigma-Aldrich, USA; Acrylic acid (AA) and acrylonitrile (AN) were obtained from Yakuri Pure Chemicals Co., (Osaka, Japan). 2,2-azobisisobutyronitrile (AIBN) was purchased from Junsei Chemical Co., Ltd. (Japan); Dimethylsulfoxide (DMSO) were obtained from Duksun Pure Chemical Co., (Korea);. DMEM media supplemented with 5 % of FCF serum, 1% penicillin / streptomycin, 1% glutamine and 0.2% amphotericin was from Sigma Aldrich, UK; Trypsin EDTA used was also from Sigma Aldrich, UK.

Preparation of zinc oxide based PAN-co-AA composite sheets

Initially 1% of zinc oxide based PAN-co-AA composite (ZnOC) sheets was prepared by adding 4.95 mL of PAN-co-AA solution into a centrifuge tube containing 0.05 g of zinc oxide nanoparticles powder and thoroughly mixed by physio-mechanical techniques. First, the centrifuge tube was placed into the vortex (VLLP SCIENTIFICA, S. Korea) for 13 min at 2000 rpm. After vortexing, the same tube was placed in the sonication using a sonicator (405, HWASHIN technology SEOUL, KOREA) for 15 minutes at 30°C to remove air bubbles from the solution. The uniform suspension ZnO and copolymer (PAN-co-AA) was transformed into the composites sheets by sol-gel method. The synthesized composites sheets were washed with distilled water.

The same procedure was applied for synthesis of 5, 10, 20, 30 and 40% (w/w) ZnOC sheets except for changing the amount of ZnO in the copolymer solution.

Thermal treatment of PAN-co-AA (Control) and zinc oxide based various composite sheets

Rectangular strips from already synthesized copolymer PAN-co-AA and various ZnOC sheets were dipped in distilled water for 24 h and their wet weights were measured by using Analytical balance (SHIMADZU, TX323L). To find out the effect of temperature on the composite sheets these were kept in a pre-heated drying Oven (DSO-300D, DMS Wisconsin, USA) at 110°C for about 30 min. After 30 min, the sheets were taken out of the oven and the rectangular strips were weighed again to measure their dry weight and to observe the possible physical changes in their structure due to effect of heat.

Scanning Electron Microscopy (SEM)

The SEM images of virgin PAN-co-AA copolymer and various ZnOC sheets were obtained by means of a scanning electron microscope 20 KV JOEL Model JSM (Japan).

Fourier Transform Infrared (FTIR) and (RAMAN) Spectroscopy

FTIR spectra were taken using a Nicolet S10 FTIR spectrometer (Thermo Scientific, USA). The range of light was from 400 - 4000 cm^{-1} and the mode of the instrument was Attenuated Total Reflectance (ATR) mode.

Raman spectroscopy was performed on Witec Raman microscope. The excitation source was laser in 532nm and the energy of excitation was 2.33 eV. The composite pieces were placed in the path of light for about 60 sec and light used was in the range (500-3000 cm^{-1}).

Thermal analysis

The thermogravimetric analysis (TGA) and differential thermal analysis (DTA) analysis of all the composite sheets were conducted on a thermobalance by heating the sample from ambient temperature to 1000 °C at 10 °C/min in a N_2 flow. TG and DTG curves of PAN-co-AA various ZnOC sheets were obtained from the analysis.

X-ray Diffraction Analysis

X-ray diffraction analysis of the composite sheets was done by X0 Pert PRO machine of PANalytical between 2h of 10–35. The machine was in the reflection mode. For the analysis the composites were cut and small pieces were made and then placed in the powder sample stage for analysis.

Physical tests

Water Swelling ratios of copolymer PAN-co-AA and various ZnOC sheets was studied by the adsorption of distilled water in different time intervals from 1 min to 4 days (6000 min) at room temperature and their weights

were measured in different time intervals. The swelling ratio was calculated by the given equation:

$$\text{Swelling ratio} = \frac{M_t - M_o}{M_o};$$ (i)

whereas M_o shows the initial weight and M_t the final weight.

Water evaporation rate of copolymer PAN-*co*-AA and various ZnOC sheets was studied by taking out the strips of PAN-*co*-AA and various composite sheets from water in different time intervals ranges from 1 min to 2 days at ambient temperature and their weights were measured. The water evaporation values for all the samples were calculated using the following equation:

$$\text{Water evaporation rate} = \frac{W_t}{W_o} \times 100$$ (ii)

whereas M_o and M_t are the weight of the sample at initial and final state, respectively.

Water holding capacity (WHC) of copolymer PAN-*co*-AA and various ZnOC sheets was calculated using the following formula.

WHC = Wet weight - Constant dry weight/dry weight (iii)

Biocompatibility of zinc oxide based composites

Biocompatibility of all the produced ZnOC with 1% to 40% ZnO content was investigated by using cultured human oral fibroblasts (passage 4) as well as cellular response was also observed by using standard MTT assay protocol. DMEM media supplemented with 5 % of FCF serum, 1% glutamine, 1% streptomycin/penicillin and 0.2% amphotericin was used for Cells culturing. Moreover, cells were permitted to confluent (100%) over the surface of tissue cultured plate and were detached by using trypsin EDTA. Cells were seeded into wells of 24 well plate having test sample seeding density of 2.0×10^4 cells / ml. The procedure was applied to material and non-material control for comparative study. Cells were incubated in a 5 % CO_2 atmosphere at 37°C for 24 hrs.

MTT assay was performed for quantitative measurement on all prepared samples. 1 ml of MTT solution was aseptically added to each well and was kept at 37°C for 40 min in incubator. Cells were then lysed with Isopropanol. The intensity of colored solution was measured by means of a spectrophotometer at a wavelength of 570 nm.

Results and discussions

Effect of mild heating on composite sheets

The digital photographical images of rectangular strips cut from PAN-co-AA copolymer and various zinc oxide based composite sheets dried at 110 °C are given in the Figure 1. Among all the samples, PAN-*co*-AA possess a high degree of expansion 16. A dramatic increase in the thermal resistivity can be viewed in the images with

increase in the quantity of ZnO content in the virgin PAN-*co*-AA copolymer. It can be seen from images that more distortion occurred in the sheets with high copolymers content and small quantity of zinc oxide.
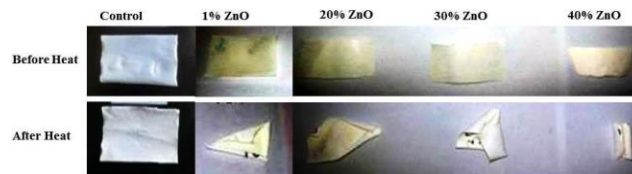

Fig. 1. Photographical images of PAN-*co*-AA and various ZnOC sheets dried at 110 °C.

FTIR and Raman spectroscopic studies of PAN-co-AA and ZnOC

The FTIR spectrum of PAN-*co*-AA is taken in the wavenumber range from 400-4000 cm⁻¹ and shown in **Fig. 2a**. The FTIR spectrum of virgin PAN-*co*-AA copolymer exhibited the typical bands at 2923, 2243, 1436 and 1719 cm⁻¹, that corresponds to C-H bending, C-N stretching, CH_2 bending for polyacrylonitrile parts and C-O stretching for AA parts, respectively. In addition, the band appeared at 3520 cm⁻¹ region is because of the OH stretching vibration that is from free carboxylic acid of the copolymer as reported by [15].

The FTIR spectra of 1% and 40% ZnOC sheet are given in the **Fig. 2b**. In case of 1% ZnO based PAN-co-AA composite the characteristic bands appeared at 3387.5, 2920.6, 2847.8, 2250, 1608.1, 1447.8, 1404.4, 1083.1 cm⁻¹ corresponds to OH, CH_2, $C \equiv N$ stretching, N-H and CH_3 bending for PAN segments and C-O stretching for A-A segments, respectively.
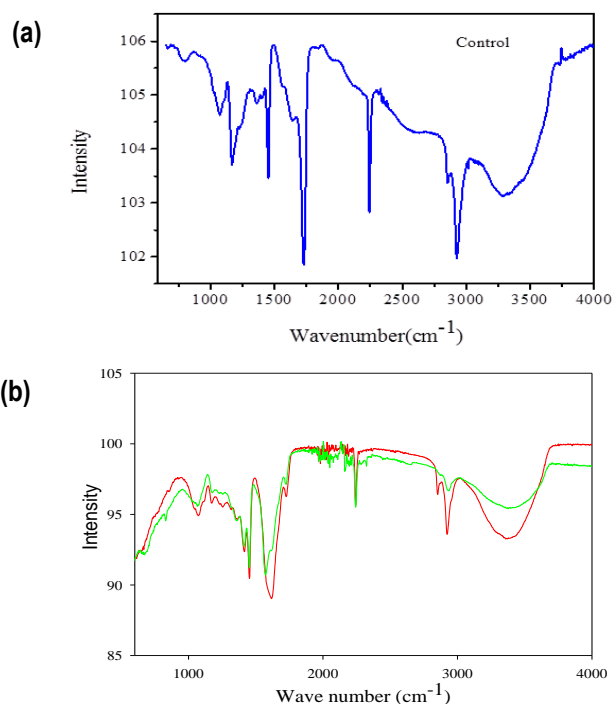

Fig. 2. FTIR spectra of (a) PAN-*co*-AA and (b) 1% (red) and 40% (green) ZnOC sheets.

Similalrly, the FTIR spectrum of 40% ZnOC the characteristic bands at 3387.5, 2935.3, 2250, 1739.7, 1579.4, 1462.5, 1419.1, 1346.3, 1069.1, 835.3, cm^{-1} corresponds to OH, CH$_2$, $C \equiv N$ stretching, C=O stretching (for AA), N-H, CH$_2$ bending and NO$_2$, R-O and C-N Stretching, respectively.

It is clear from the comparative study that after the incorporation of 1% and 40% ZnO into the PAN-*co*-AA (Control) no new bands were observed which is an evidence that it did not changed the chemical structure of the resultant polymer composite.

The raman spectra of 1% and 40% zinc oxide based composite showed the appearance of only one broad peak centered at 2121.34 cm^{-1} with intensity 4080 which confirmed the presence of PAN-co-AA. In the spectra there were few defused additional peaks appeared at the range 100-600cm^{-1} which indicates the presence of ZnO in the polymer matrix [16].

Thermal Analysis of zinc oxide based composite sheets

The TG and DTG curves of 1%, 5%, 10%, 20%, 30% and 40% zinc oxide based composite sheet are also shown in **Fig. 3a** and **Fig. 3b,** respectively. The **Fig. 3a** indicates that there is a weight loss for all the composite sheets at around 234°C to 269°C. This is possibly attributed to desorption of small amount of physisorbed water. The thermal degradation caused a weight loss in the PAN-*co*-AA copolymer which comes in the range of 349°C to 614°C. This corresponds to the appearance of two DTG peaks; one centered at 304 °C and the other at 567 °C (Fig. 3b), indicating that thermal degradation of the PAN-*co*-AA copolymer occurred in two steps. The first one is from 257°C-377°C with greater speed of degradation at 325°C while the second one is from 400°C-625°C with maximum degradation speed (weight loss) at 521°C. Among the two steps for degradation, the first exotherm as revealed from DTG analysis is corresponds to decomposition of AA into anhydride by removal of water from the acid group. Further decomposition of the anhydride is accomplished by decarboxylation. In the meantime, AN also undergo through the process of dehydrogenation and stabilization by cyclization. However, these thermal transformations are overlaid by the decomposition of AA.

In the second step of degradation and appearance of exothermic peak at DTG, AN undergoes aromatization from 400°C - 625°C as reported by Dima et al [17].

As shown in **Fig. 3a,** the thermal degradation of all the composite sheets taken place in the temperature range from 234 to 600°C. This range is the same as appeared for PAN-*co*-AA. This might be due to the fact that zinc oxide is thermally stable up to 600°C. No change in weight loss is in the TG curves of various composite sheets by the incorporation of zinc oxide is attributed to the high thermal stability of ZnO as reported by 12. However, the DTG curves of some composite sheets i.e 30% and 40% show a slight different behavior from the other composites. DTG **(Fig. 4b)** curves show that increasing ZnO amount, the peak for second step of degradation that

occurs due to AN decomposition decreases from DTG curves of 30% and 40% composite sheets. This is because of the excessive amount of zinc oxide that provides thermal stability to the composite sheet by preventing degradation of acrylonitrile.
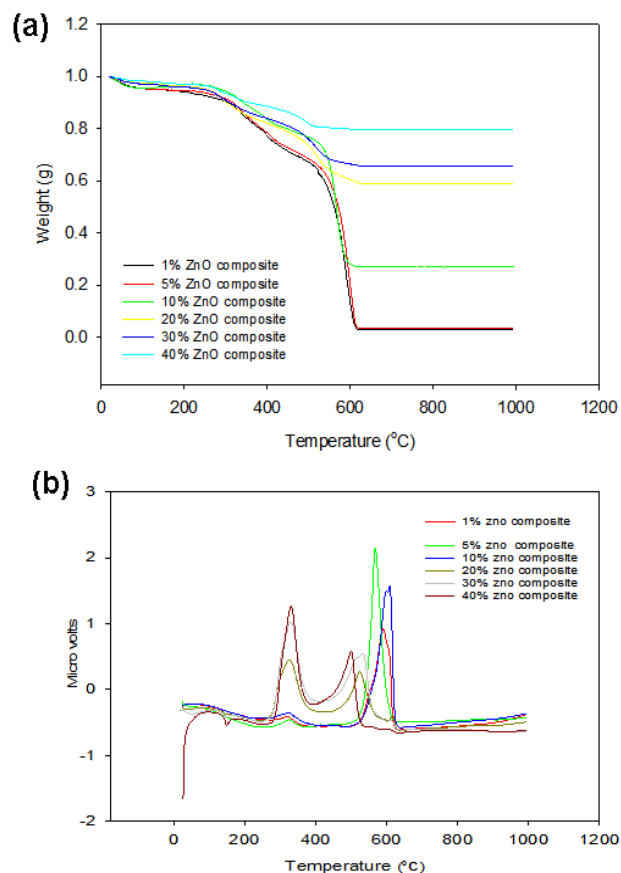

Fig. 3. (a) TGA and (b) DTG curves of various ZnOC sheets.

SEM analysis

To find out the relative differences between virgin PAN-*co*-AA copolymer and various ZnOC sheets SEM micrographs were used. The distribution of the ZnO nanoparticles and its effect on the PAN-*co*-AA copolymer was determined. It can be seen from the **Fig. 5** that the top view of PAN-*co*-AA film is a three-dimensional porous structure. After the incorporation of ZnO, the morphology of copolymer was significantly changed, with the formation of homogeneously distributed ZnO sheet as reported 15. The micrographs taken at 10 micrometer and 1 micrometer clearly show the ZnO dispersion in it. The dispersion of ZnO was relatively good but with the gradual increase in the zinc oxide content (above 20%) into the copolymer caused aggregation of the ZnO particles.

XRD analysis

The XRD pattern of the PAN-*co*-AA (control) given in Table 1 indicates an intense diffraction peak occurred at 2θ value of 19.39^0 and 21.72^0 which correspond to the

crystalline structure of the polymer with slightly amorphous nature. The XRD pattern of the PAN –co-PAA showed double peak formation which confirmed copolymer formation. The polyacrylonitrile stabilize itself within the amorphous polyacrylic acid[18]. The XRD pattern for different percentage ZnOC sheets is shown in the **Table 1**. The XRD data of these composite sheets showed the appearance of some additional new peak at 2θ value of ~30.99^0, 32.09^0, 32.32^0 as well as 36.49^0, 36.65^0 and 36.65^0 in case 1% ZnOC, 20% ZnOC and 40% ZnOC respectively, which are according to the values that are given in literature and confirm the incorporation of zinc oxide in the copolymer[19]. Therefore, it is concluded that the introduction of zinc oxide has changed the original structure of PAN-*co*-AA.

Table 1. 2θ values in XRD pattern of PAN-*co*-AA (control) and ZnOC.

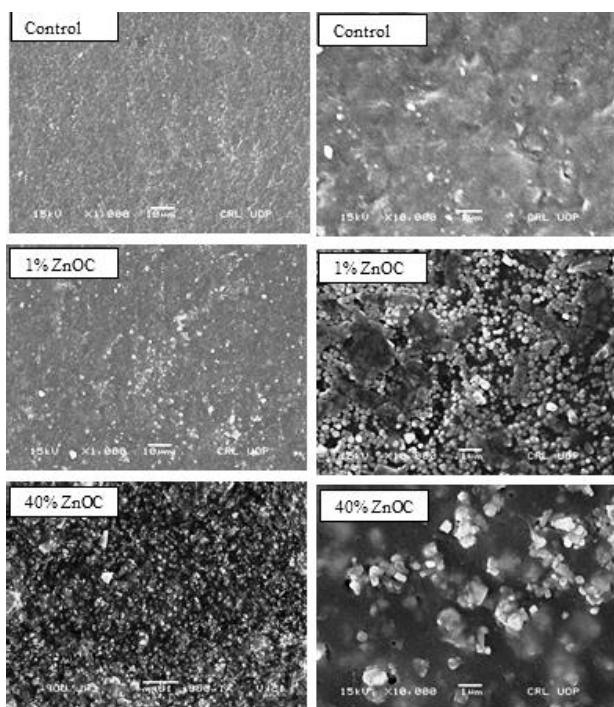| 2 θ values			
Control	**1%ZnOC**	**20%ZnOC**	**40%ZnOC**
19.39	20.24	20.33	22.65
21.72	31.99	32.09	32.32
-	36.49	36.65	36.65

Fig. 5. SEM micrographs showing surface morphology of control, 1 % and 40% ZnOC sheets.

Swelling Ratio (SR), Water evaporation rate (WER) and Water holding capacity (WHC) of ZnOC sheets

Fig. 6a shows a comparison of swelling ratios of various zinc oxide based PAN-*co*-AA composite sheets in water at different time intervals ranging from 1 min up to 4 days (6000 min) at room temperature.
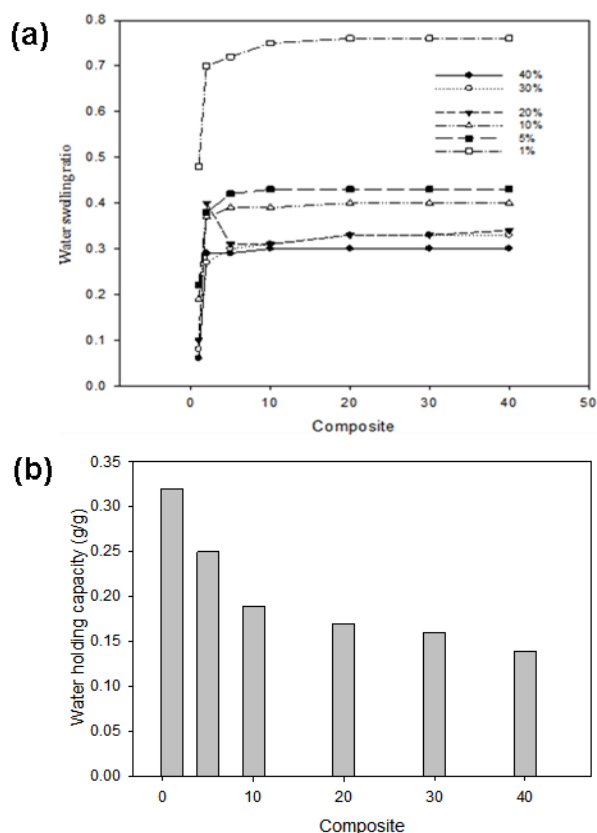

Fig. 6. Physical properties studies (a) Swelling ratio and (b) WHC of PAN-*co*-AA various zinc oxide based composite sheets.

The **Fig. 6a** clearly shows that the maximum swelling is obtained for composite containing less amount of zinc oxide as compared to higher content. This deviation in swelling ratio is due to the presence of more hydrophilic groups such as AA and AN [20, 21] in the polymer composite. The addition of more ZnO (which is hydrophobic) into PAN-*co*-AA matrix reduces the amount of hydrophilic groups in the copolymer which decreases the mutual action between water and hydrophilic groups of the copolymer. It is concluded that the internalization of hydrophilic or hydrophobic groups in the copolymers can manage the behavior of phase transition as reported by Seddiki and Aliouche [22]. The swelling rate is faster in the first 90 min and become slower and steady when reaches to 6000 min.

Water evaporation rate of various ZnOC sheets was performed after soaking the sheets for 4 days. The rate of evaporation was measured by different time intervals ranging from 1 min to 2 day at room temperature. The water evaporation rate study showed that maximum water evaporation ratio i.e. 60 was obtained for 40% composite sheet while less evaporation ratio was observed for ZnOC with 1% ZnO content.

WHC of various ZnOC sheets was obtained after drying their completely swelled wet (until no change in weight occurred) sheets at room temperature.

The **Fig. 6b** for WHC clearly shows that the maximum WHC is achieved for PAN-*co*-AA (control) as compared to the ZnOC sheets. This is due to the fact that

both monomers AN and AA in the copolymers are hydrophilic in nature. The absorption capacity increases with the increase in the quantities of both AN and AA. The enhancement of absorption capacity due to the AN is reported by Kiatkamjornwong *et* al 21. The hydrophilic nature of AA is reported by Mahdavinia *et* al 22. However, as the amount of ZnO increased in the copolymer matrix it can be noted from the Fig that it resulted in a sharp decrease in WHC when the incorporation of ZnO content were increased from 20% to 40% in the as prepared ZnOC.

Biocompatibility study

Cell viability of all produced ZnO based scaffold samples along with 1% to 40 % concentration respectively, was studied quantitatively with standard MTT assay protocol. Decreased cellular response was observed on ZnO based scaffold samples along with 1%, 5%, 10%, 30% and 40% concentration respectively, studied in this research. However, signs of significant biocompatibility by a confluent sheet of cells over the surface of tissue cultured plate were observed particularly on 20 % concentration ZnO based scaffold sample and was quantitatively supported by MTT results as shown in following **Fig. 7a** and **Fig. 7b.**
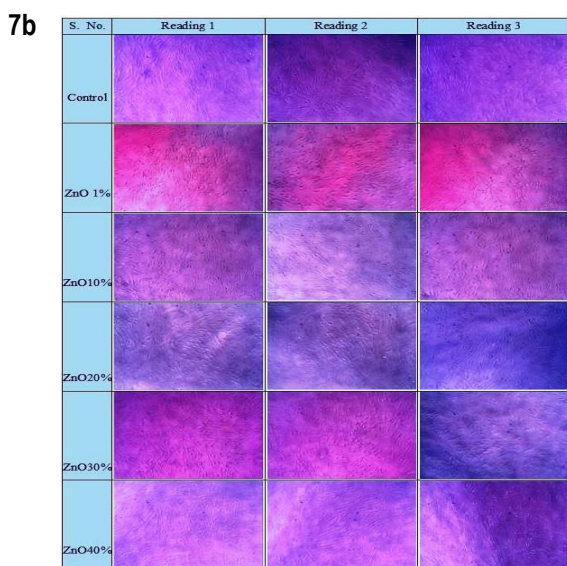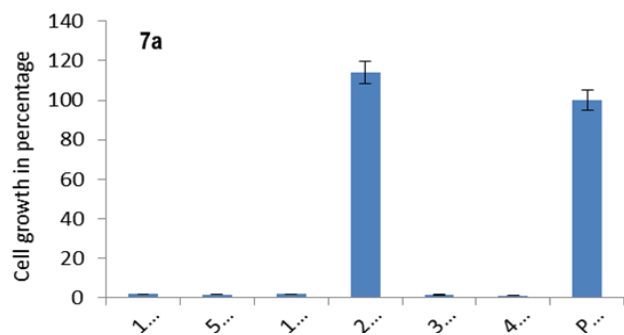

Fig. 7. (a) Cell viability results with MTT assay of control and ZnOC (1-40%) and (b) microscopic images of 24 well plates after 24 hrs of incubation of human oral fibroblasts at 37°C, before performing MTT assay analysis along with sample immersed medium.

In general, all obtained results are more consistent of material with decreased solubility therefore, decreased ion release into cell medium occurred. This could create unfavorable effect over the normal growth of cells as shown in **Fig. 7b**. Moreover, release of ZnO ions with 20 % concentration potentially encourages the process of osteo-integration by depressing bone resorption and also promotes further bone formation.

Conclusion

In this work 1%, 5%, 10%, 20%, 30% and 40% zinc oxide based P(AN-co-AA) sheets were synthesized by Casting and sol-gel method. The SEM micrographs showed uniform dispersion of zinc oxide in the copolymer but with gradual increase of zinc oxide content cause its agglomeration in the copolymer and lower its homogeneous distribution. The XRD pattern, FTRI and Raman spectroscopic studies justified zinc oxide incorporation in the copolymer. The results of TGA and DTA showed thermal stabilization of the prepared composites due to zinc oxide addition. Physical tests like swelling ratio, water evaporation rate and water holding capacity of the prepared composites were greatly changed with addition of ZnO nanoparticles in the copolymer matrix. It is concluded from the results that the introduction of ZnO brought hydrophobic character to the copolymer.

The results of the biocompatibility study made it clear that the ZnOC have a meaningful effect on the cells with 20% ZnO content. While a decrease effect was observed with 1%, 5%, 10%, 30% and 40% ZnO content.

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