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Water and fat absorption studies of Polyvinyl alcohol-Chitosan-Boron nitride hybrid nanocomposites with enhanced thermal properties

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ABSTRACT

PVA (Polyvinyl alcohol) based nanocomposite membranes were fabricated, these composite membranes reinforced with chitosan and boron nitride nanosheets via freeze-thaw method, no crosslinking agent such as glutaraldehyde was used in the synthesis process. Swelling, fat absorption and thermal degradation studies were carried out. PVA membranes showed the highest swelling (water uptake) and PVA-Chitosan membranes exhibited the highest fat absorption, while PVA-Boron nitride nanocomposites showed least degradation in water. Scanning electron microscopy, X-ray diffraction, Fourier transform-infrared spectroscopy (FT-IR) and Thermogravimetric analysis (TGA) were done to analyse the membrane morphology and properties. FT-IR analysis revealed that good bonding was achieved between the two polymeric materials. TGA analysis revealed that there is significant increase in the thermal properties of the membranes with addition of BNNS without significant deterioration of water uptake or fat absorption performance.

INTRODUCTION

Polymer nancomposites is a term used for polymeric materials which have been reinforced with nanomaterials. There is a lot of research activity targeted towards polymer nanocomposites as they show substantial improvement in various propertiesat low concentrations of nanomaterials[1-5]. Polymer nanocomposites are being prepared for use in numerous applications such as solar energy capturing materials[6], heavy metal removal[7], dielectric materials[8], biomedical[9] and food applications[10].

Polyvinyl alcohol (PVA) is a biodegradable, nontoxic, hydrophilic and biocompatible it has been used for many biomaterial applications[11,12]. PVA is used in many forms; hydrogels[13], fibres[14], and thin films[15], including many more. Chitosan is a natural polysaccharide formed by the deacetylation of chitin which is obtained from the shells of crabs and shrimps[16]. Chitosan is relatively non-expensive, biocompatible, non-toxic, and it can be easily blended with other materials, which gives rise to applications in food, medicine, waste-water and cosmetics[17-21]. PVA- Chitosan composites have been studied extensively for their use as biomedical materials[22-25]. PVA and Chitosan composites are fabricated using various techniques; freeze thaw[26], chemical cross-linking[27], electrospinning[28]. Swelling studies of PVA-Chitosan composites have been studied extensively[24,28]. Fluid uptake is an important parameter in the ability of a material to be used for biomedical applications. PVA-Chitosan composites have a good ability to uptake fluid and hence are being developed for use in oral drug delivery and tissue engineering scaffolds. Chitosan is known to be a good absorber of lipids[29].

Hexagonal boron nitride has recently been attracting a lot of interest for its several desirable qualities such as high thermal stability, chemical inertness, good resistance to oxidation, which allows it to be used in medical, optical, catalytic, and electrical insulation[30-32]. It is has also been used to improve the mechanical properties of polymers[33]. Boron nitride is also known to noncytotoxic properties[34].

In the current work we have employed the use of Boron nitride nanosheets (BNNS) to improve the thermal properties of PVA-Chitosan nanocomposite material, and studied the effect of BNNS on the fluid and fat absorption of the nanocomposite material. We envisage that increased thermal stability coupled with good absorption properties will open new avenues for the use of PVA hydrogels in various fields, especially in biomedical applications.

EXPERIMENTAL

Materials and methods

Polyvinyl Alcohol (Molecular Weight, M_w -115000 with degree of hydrolysis of 98-99%), hexagonal Boron nitride (h-BN), Dimethylformamide (DMF), and Acetic acid were procured from Fischer Scientific. Chitosan from Sisco Research Laboratories with degree of de-acetylation 85% and density 0.4 g/cc. Glacial Acetic acid was used to dissolve Chitosan. All chemicals were used without further purification.

Boron nitride nanosheets were fabricated in a two-step method. Firstly, h-BN was sonicated for 48 hrs. inDMF. This solution was then centrifuged at 9000 rpm for 6 hours. The supernatant was collected and dried under vacuum at 100°C for 24hrs.

Boron nitride filled aqueous solution of Polyvinyl alcohol (PVA) was prepared by dissolving PVA powder in distilled water stirred at 80°C for 2 hrs. followed by sonication for 30 minutes at room temperature. Concentration of nanosheets was kept at 1wt. % of PVA. Chitosan was added to another aqueous solution of 1% acetic acid and mixed on magnetic stirrer for 1 hr. Two solutions were mixed and were further subjected to mild stirring for 30 mins to get a homogeneous blend. The prepared solution was poured intomold and subjected to repeated freeze thaw cycles three times consisting of freezing at -10°C for 8 hrs and thawing at room temperature for 15 hrs. Thereafter specimens were dried at 40°C under vacuum for 24 hrs

Four membranes viz. PVA, PVA-BNNS (1wt. %), PVA-Chitosan (10 wt.%), and PVA-Chitosan (10 wt%)-BNNS (1 wt%) were fabricated in total.

Characterization studies

(a) Swelling and degradation index

Pre-weight dry membranes of different compositions were put into distilled water and allowed to reach equilibrium for 24 hrs. at room temperature at neutral pH. Swollen membranes were removed from water and whipped with filter paper and weighed again immediately. Swelling ratio is calculated as

$$\mathbf{S.\ R.} = \frac{\mathbf{W_s - W_d}}{\mathbf{W_d}} \times \mathbf{100}$$

Where W_d and W_s represent the dry and swollen specimen respectively.

Swelled membranes were then dried at room to evaluate how long the membranes can hold water to study de-swelling index.

Degradation indexwas calculated using the following formula

$$\mathbf{Degradation\ \%(age)} = \frac{\mathbf{W_d}}{\mathbf{W_i}} \times \mathbf{100}$$

Where W_d is the weight of membrane after de-swelling and W_i is the initial weight of the membrane before swelling tests.

(b) Fat absorption studies

Pre-weight membranes of different compositions were added to 5 cm^3 of butter oil for an hour. After an hour, the gels was taken out and dried in the air and excess oil was cleaned off by wet filter paper followed by dry. The weight of the specimen was measured again by the weighing balance. The result was recorded to calculate the amount of oil that had been absorbed.

(c) Thermal, structural and microstructure analysis

X-ray scattering techniques were used to get information about the structure and physical properties of membranes. This was performed by Bruker made D-8 ADVANCE Powder X-ray diffractometer at room temperature. The X-ray scan was made over a range of 2θ values of 10–80°. The Thermogravemetric Analysis was carried out on Mettler Toledo model TGA/SDTA 851 from room temperature to 500 °C in air at a heating rate of 10 °C/min. For FTIR studies, the powdered specimens were ground with potassium bromide (KBr) as diluents and pressed into a pellet. The 514 nm argon ion laser excitation was used to scan the samples from 500 cm^{-1} to 4000 cm^{-1}. Microstructure studies of the membranes surface was examined by Scanning electron microscope (SEM, model LEO 440) for microstructure studies.

RESULTS AND DISCUSSION

Figure 1 shows the characteristic FT-IR of PVA, Chitosan (CS) and PVA-Chitosan blend. FT-IR was used to determine the chemical groups of the polymers. PVA exhibits peaks at 2940, 1448, 1248, 1095, and 847 cm^{-1} which are related to (CH_2), (CH-OH), (CH), (C-O) and (C-C) respectively[35]. Chitosan membrane showed peaks around 898 and 1151 cm^{-1} which are peaks exhibited by repeating saccharide structure of chitosan, a weaker peak at 1255 cm^{-1} is attributed to amino group, and another peak at 1383 cm^{-1} is assigned to CH_3 symmetrical deformation[35]. The appearance of a peak at 3445 cm^{-1} indicates that hydrogen bonding has taken place between chitosan and PVA polymers causing OH/NH_2 stretching[36]. Peaks at 1721, 1635 and 1418 cm^{-1} may be due to carbonyl stretching, absorption of $NHCOCH_3$ groups and C-H bonds respectively, in the PVA-chitosan blends[36-38].

Figure 2 represents the XRD peaks of PVA, PVA-BNNS (1 wt %), PVA-Chitosan and PVA-Chitosan-BNNS composites. XRD peaks of PVA are seen at 2ô 20° and 40°. The sharp peaks of PVA show that it has a high level of crystallinity. In contrast the Chitosan peaks are observed at 2ô 16.5°, 20° and 36°, and these peaks are very weak, indicating the low crystallinity of Chitosan. The intensity of the PVA peaks can be seen to get lower as it is blended with Chitosan, this is consistent with research carried out by other groups. This may mean that there has been an interaction between the two polymeric materials[39].

Figure 3 shows the thermal decomposition process of the different membranes. They show a multi-step decomposition process, this can be attributed to evaporation of absorbed water, degradation of PVA-Chitosanand subsequent degradation of remainders. The weight loss characteristic is same for all the membranes till 310°C. 60% weight loss occurs at 370°C

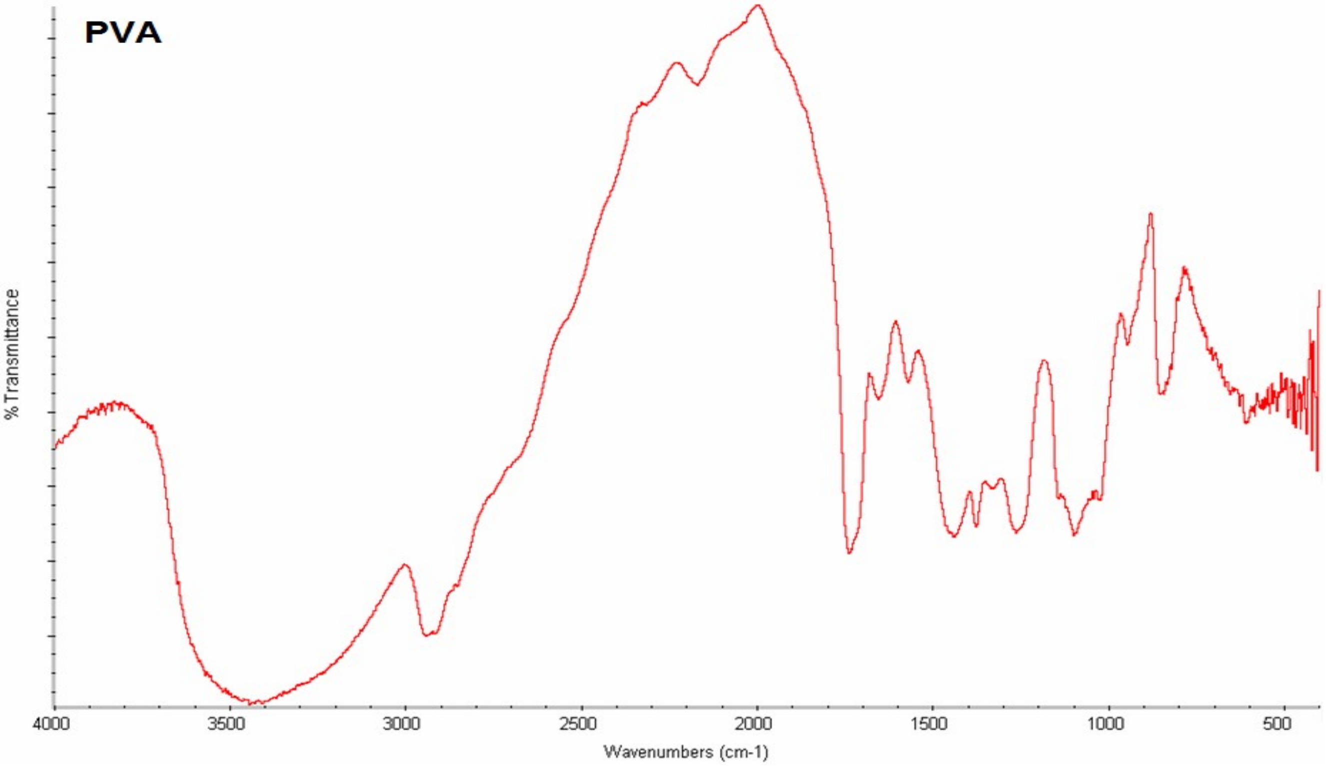


Figure 1(a) : FT-IR of PVA

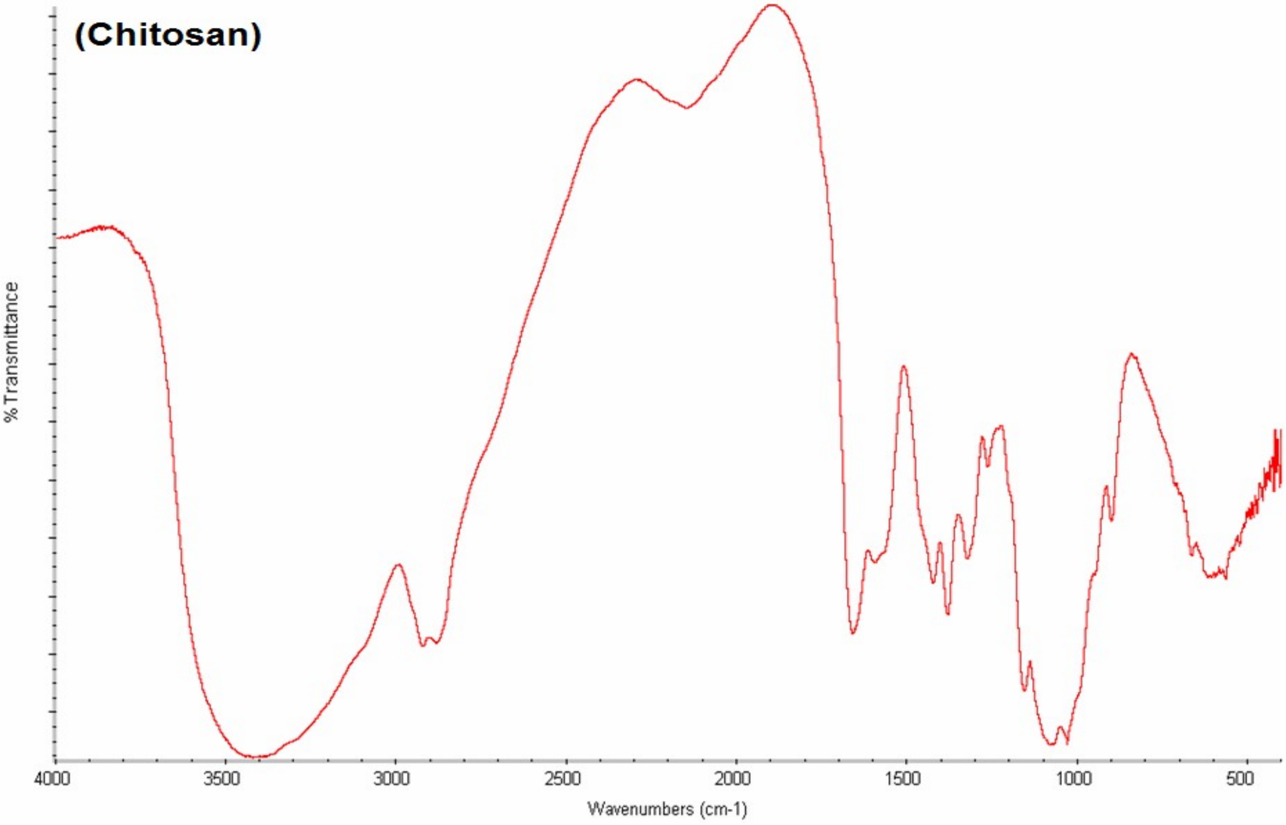


Figure 1(b) : FT-IR of Chitosan

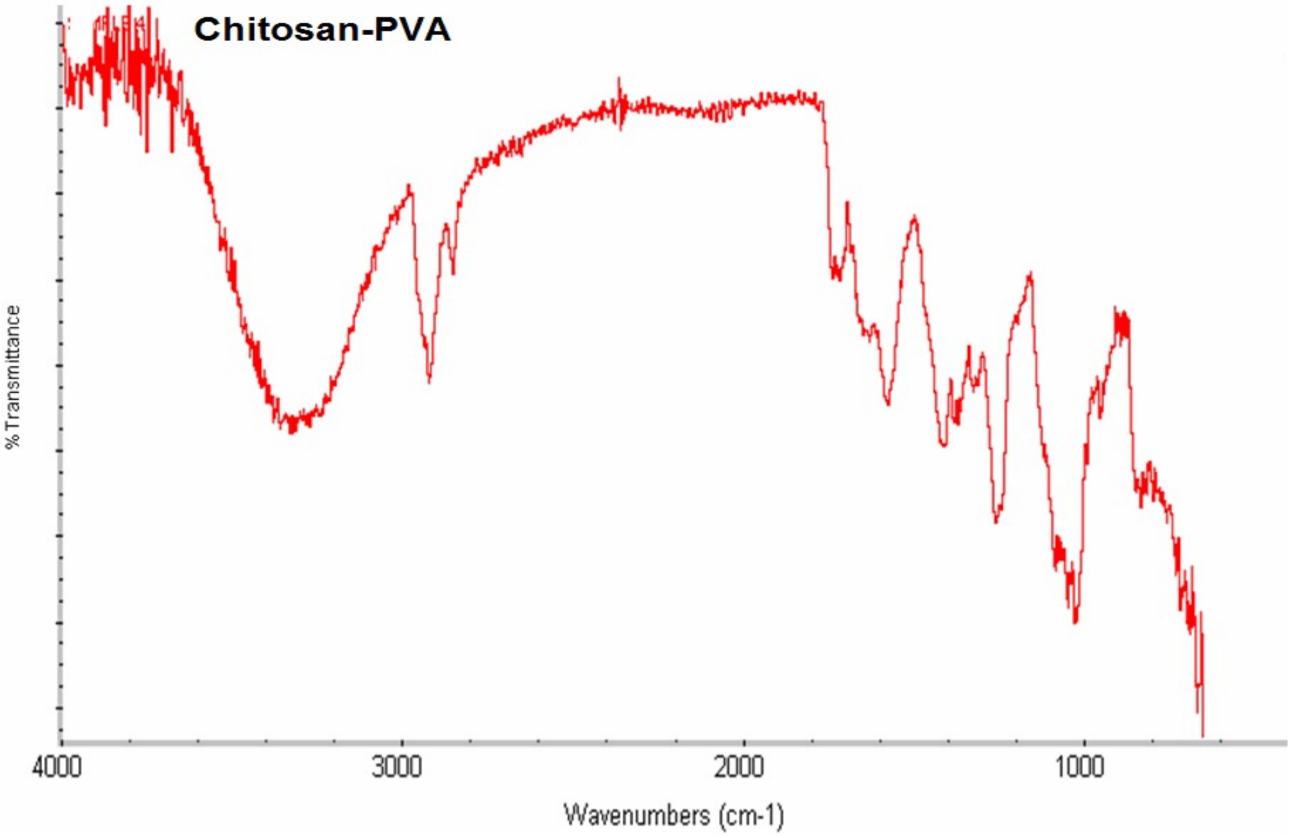


Figure 1(c) : FT-IR of Chitosan-PVA

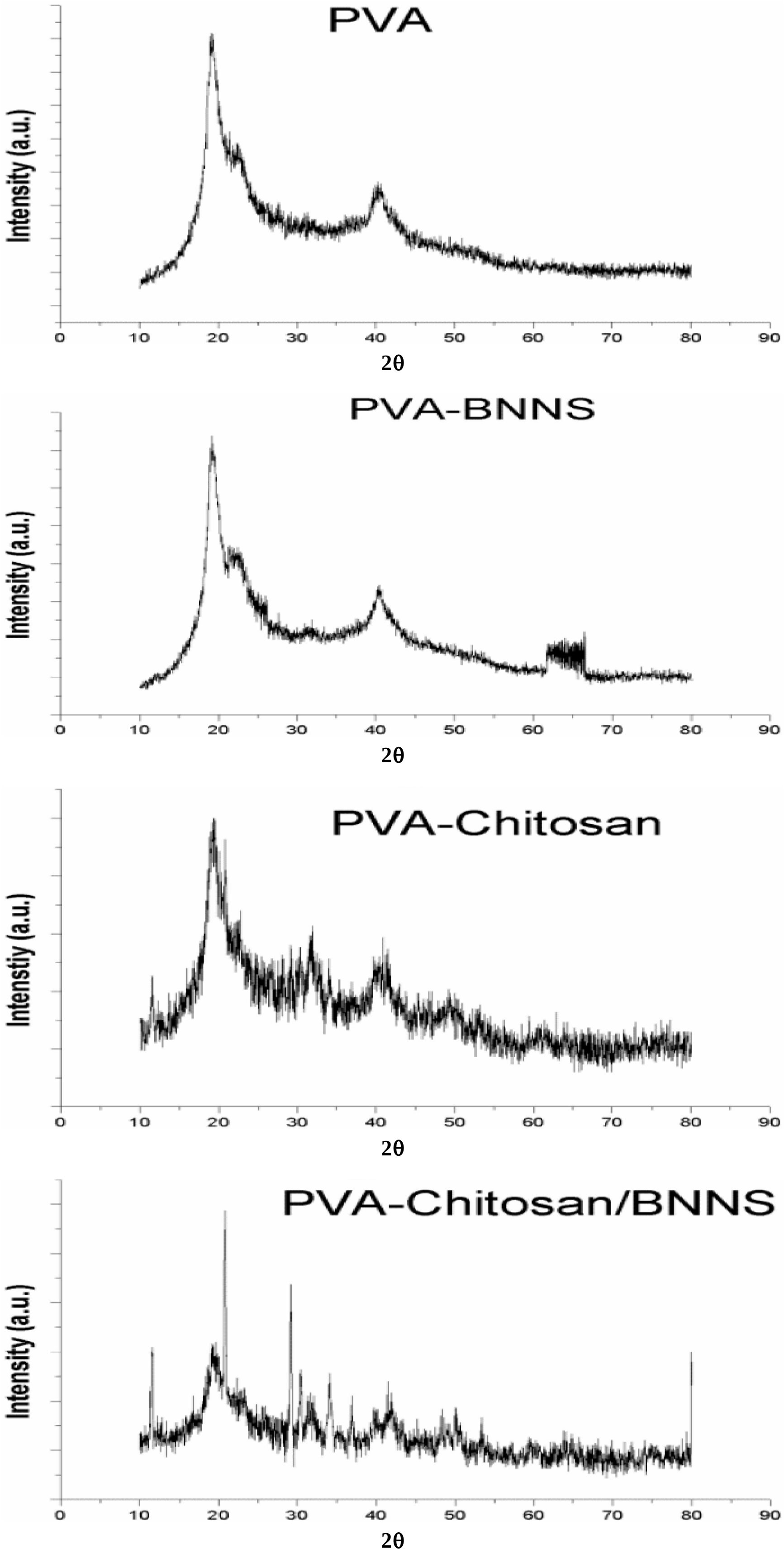


Figure 2 : XRD spectra

for pure PVA and 425°C for PVA-Chitosan-BNNS membrane, this is a significant increase of 55°C. PVA-BNNS shows an increase in thermal stability of 34°C. The thermal stability of the PVA-Chitosan-BNNS is higher than that of the PVA-BNNS membrane; this shows that there is good bonding achieved between the PVA and Chitosan polymers. It is interesting to note that the thermal properties of PVA-Chitosan and PVA-BNNS are similar until 75% weight decomposition. We suppose that the BNNS are not all available at the surface in PVA membrane to provide a thermal shielding effect. At the higher temperatures when PVA membrane has been degraded the BNNS are exposed and provide thermal shielding and hence the notable difference in thermal profiles at the higher temperatures. It is safe to say that the highest thermal stability is shown by PVA-Chitosan-BNNS membrane as expected.

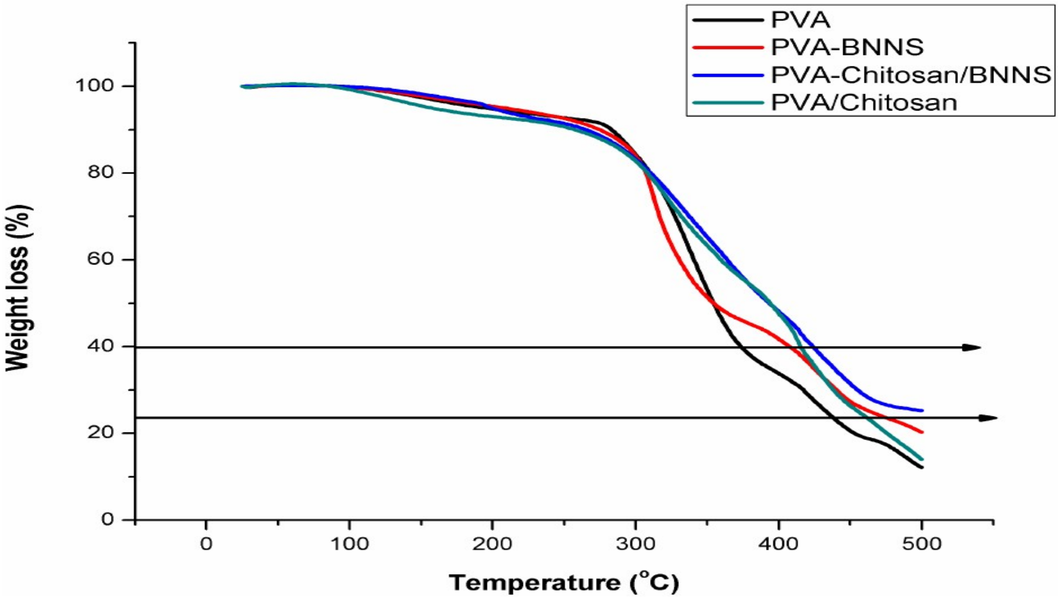


Figure 3 : TGA analysis of membranes

Figure 4 shows the swelling characteristics of the membranes. The swelling process depends on the movement of water into the open spaces in the membrane. The rate of water absorption is fairly constant. Equilibrium is achieved after 22 hours. Maximum water uptake was shown by pure PVA membrane, PVA-Chitosan-BNNS membrane showed the least water upatake. This was expected as formation of PVA-Chitosan networks causes a decrease in the hydrophilic groups of PVA and a more rigid network is formed, leading to a decrease in water uptake. BNNS has been shown to have super-hydrophobic nature[40], causing the uptake of water in the membrane to be reduced. Swelling percentage at 24 hours is summarized in Figure 5. A drop of 40% is seen for the swelling percentage.

The degradation index was also calculated. The degradation is the loss of the properties of the polymer. It can be caused by the polymer being dissolved in the solvent, the breakdown of bonding between the polymeric materials. The results are summarized in Figure 6. PVA shows the highest degradation index, with PVA-Chitosan-BNNS showing the least degradation. BNNS are resistant to chemical degradation; they provide the membranes with higher chemicalstability, leading to a lower degradation index.

Fat absorption studies were also carried out for the membranes. The highest fat absorption was observed for PVA-Chitosan membranes as expected. Chitosan is known to absorb fat and is sometimes used as a dietary supplement to observe excessive lipids[41]. Lowest absorption was observed for PVA-BNNS. BNNS takes up the free volume in the inter-polymer network and hence less fat is absorbed into the membrane. Results are summarized in Figure 7.

Figures 8 (A-C) show the scanning electron micrographs of PVA-Chitosan membranes. Figure C shows the BNNS embedded near the surface of the

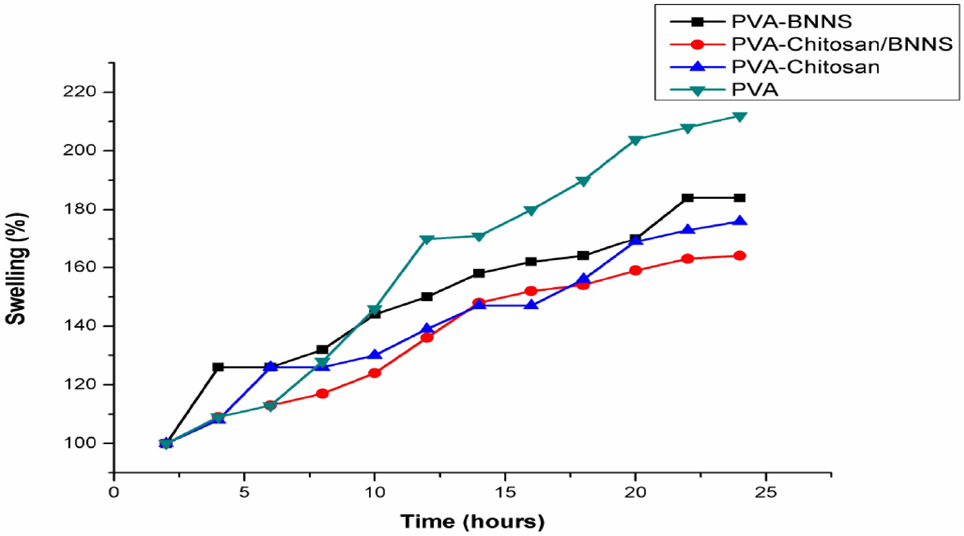


Figure 4 : Swelling characteristics of membranes

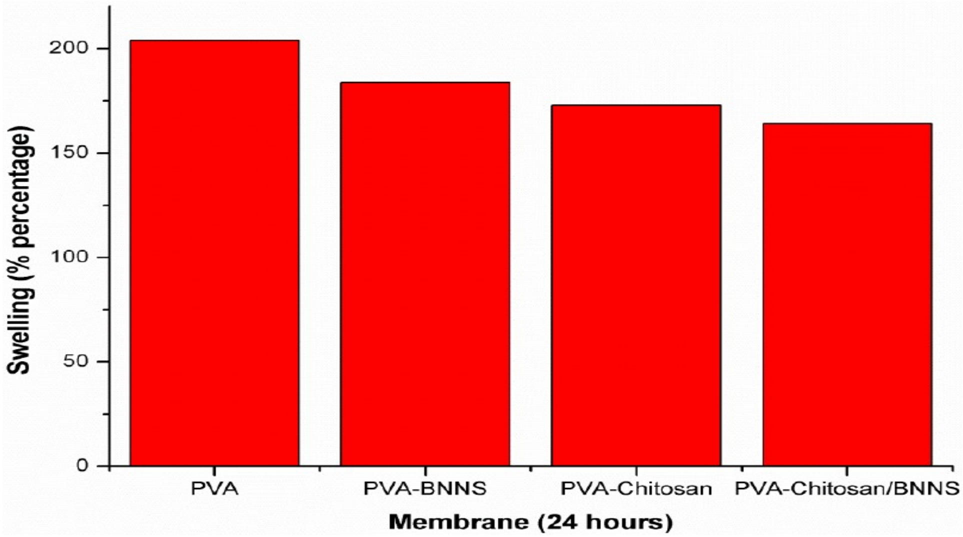


Figure 5 : Swelling % age of membranes after 24 hours

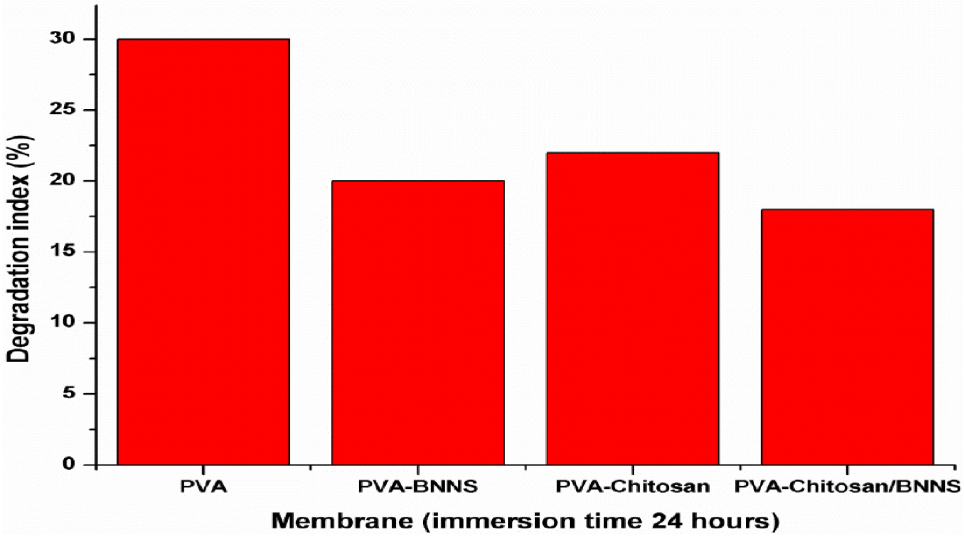


Figure 6 : Degradation index of membranes after 24 hours

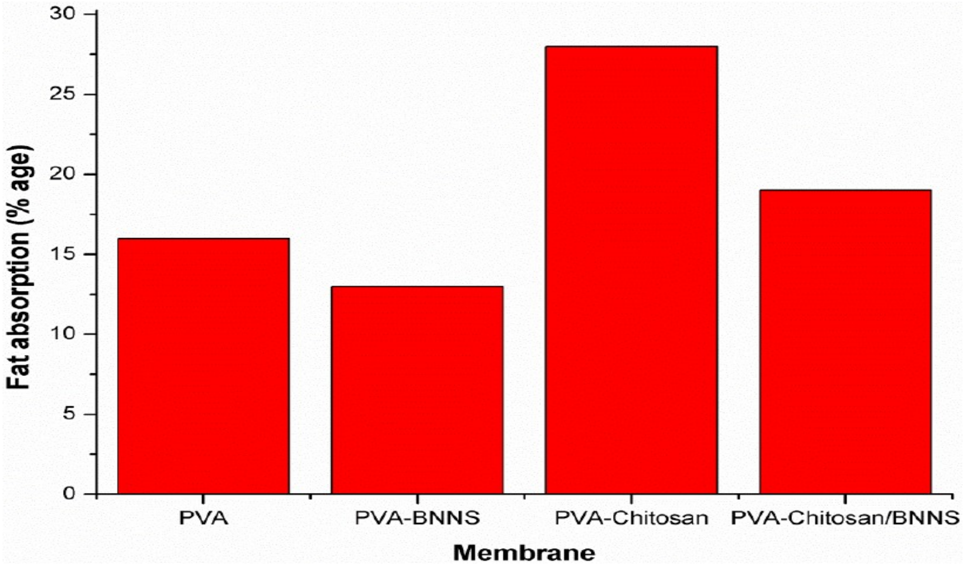
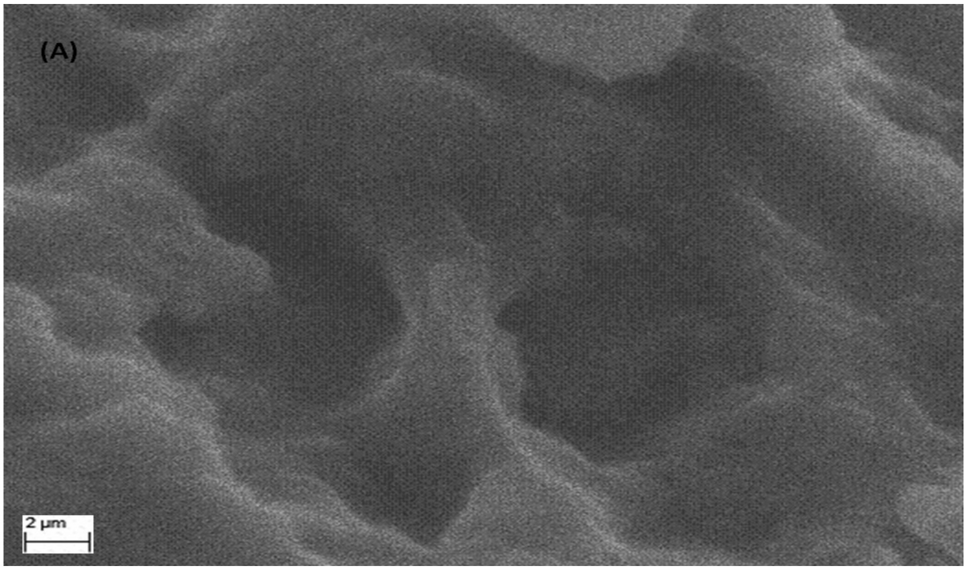
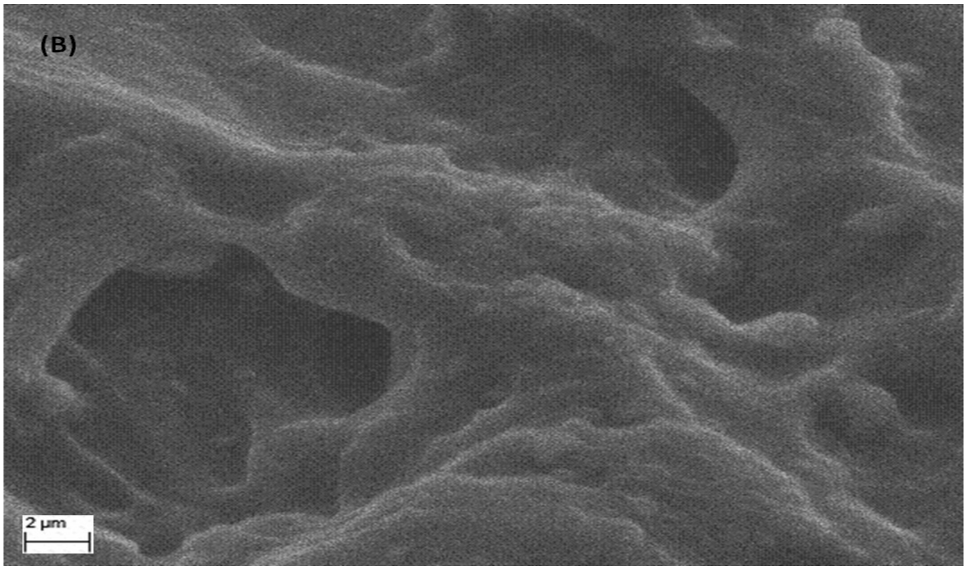
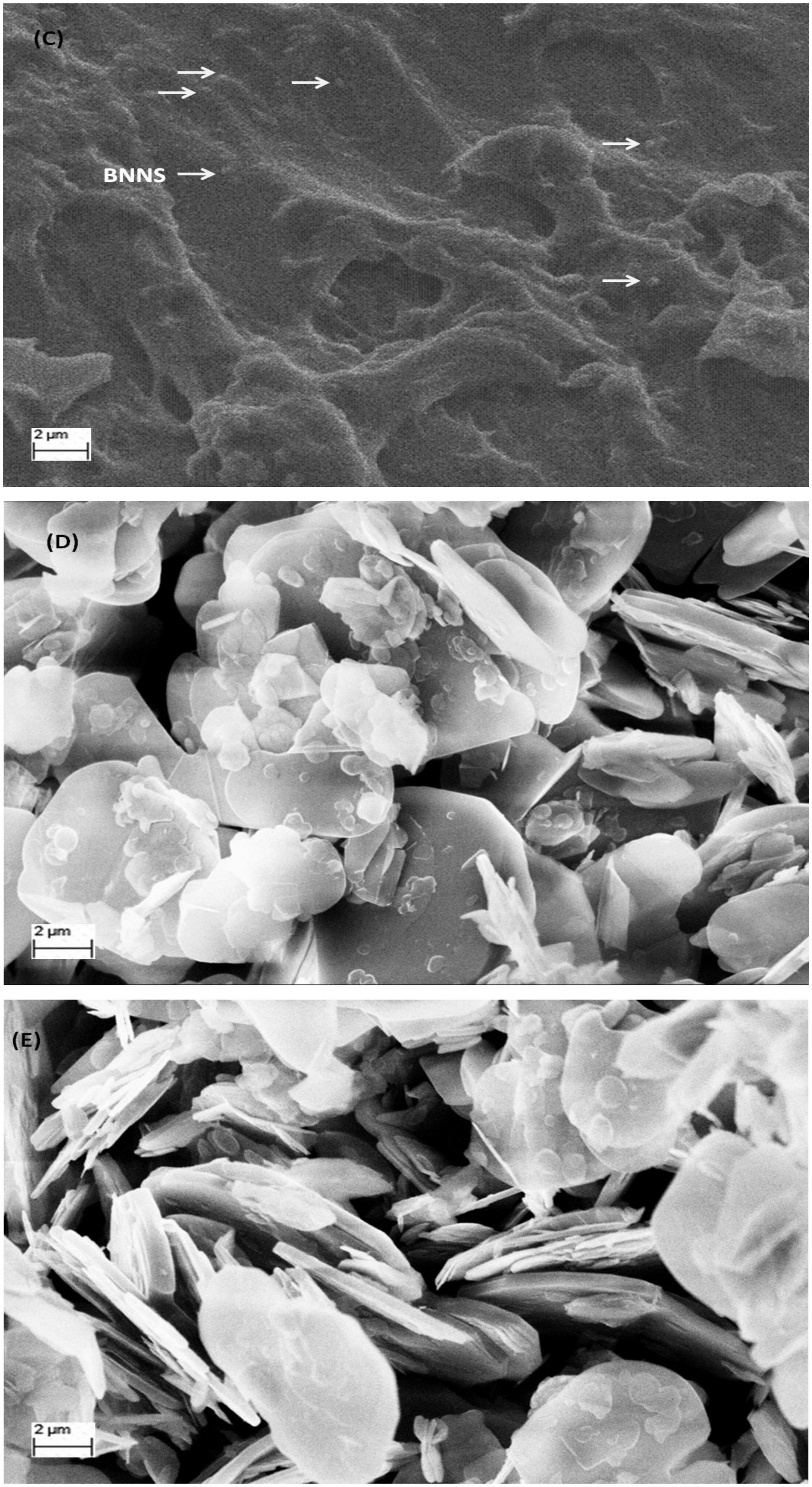


Figure 7 : Fat absorption of membranes






(C)
BNNS
2 µm
(D)
2 µm
(E)
2 µm

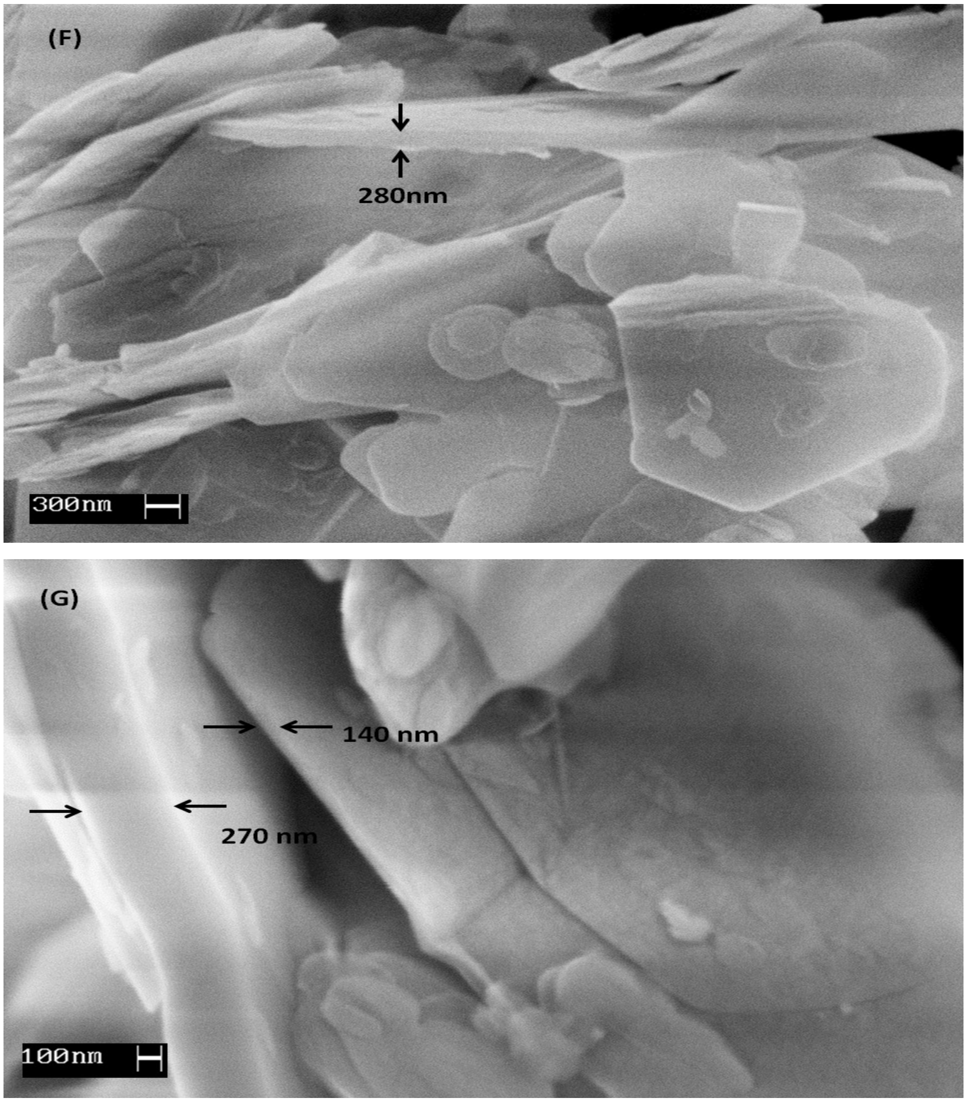


Figure 8(a-g) : Microstructure of PVA-Chitosan membrane and Boron nitride nanosheets

PVA-Chitosan membrane. The dispersion was seen to be adequate. Figures 8 (D and E) show the SEM of BNNS fabricated in this work. The sheet like morphology can be clearly seen in the SEM. Figures 8 (F and G) take a closer look at the morphology of the BNNS, the width of the BNNS was seen to vary from 100nm-300nm. Figure 8(G) shows the BNNS stacked against each other vertically.

CONCLUSION

PVA-Chitosan and PVA-Chitosan-BNNS polymer nanocomposites were fabricated. We observed that there is a significant increase in the thermal stability of the composite after addition of BNNS. The other attractive qualities of the PVA-Chitosan membranes, such as water uptake and fat absorption were not compromised significantly by the addition of the nanomaterial. We envisage that this material can be used in various applications and the increased thermal properties might open up new avenues for the material to be used in.

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