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DIFFERENT PVA-HYDROXYPROPYL GUAR GUM IRRADIATED CARBON NANOTUBE MEMBRANES FOR DIFFERENT APPLICATION

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ABSTRACT

Strong as well as flexible biodegradable membranes are of great demand in recent technology. Similar hydrophobic membranes have been developed by irradiating different weight poly (vinyl alcohol) (PVA) – hydroxypropyl guar gum (HPG) blends and followed by mixing with multiwalled carbon nanotube (MWCNT). Mechanical property and swelling-de-swelling study indicates that electron beam irradiation produces better crosslinking at low irradiation dose (5kGy) and especially in low molecular weight PVA-HPG matrix than the higher doses where chain degradation is more. Scanning electron microscopic (SEM) analysis shows that low wt% MWCNT produce finer dispersion in both PVA-HPG matrixes due to better interaction and fitment with the matrixes which is reflected in theromogravimetric analysis (TGA) i.e., thermal stability of the membranes increases. Finally the better properties of the membranes make them suitable for various applications under different condition.

Keywords: Polymer; Irradiation; Membrane; Composite; Carbon Nanotube.

1. Introduction

Biodegradable ornatural polymers draw the special attention in recent days due to increasing environmental concern, as most of the synthetic polymers are non-biodegradable and causes deleterious environmental impact. Natural polymers suffer very much in different fields due to their poor cohesive strength [1]. On the other hand, Synthetic polymers are highly effective due to their excellent combination of physical and mechanical properties, which renders their wide applicability as film wraps, plastic bags, electric insulation, toys, fabrics, pipes, paints, etc [2-4]. With ongoing advanced research in different field most of the researchers today are oriented towards designing new material from the existing one rather than discovering completely new materials. So, it has been realized to introduce biodegradable polymers for similar applications [5-6]. Thus under such circumstances the most viable option is the blending between natural and synthetic polymers [7-8]. Blending with natural polymer several compositions involving PVA and other synthetic polymers has already been explored [9].

PVA is versatile synthetic polymer having nice combination of mechanical strength, elasticity, biocompatibility, air permeability and water absorption properties [10-12]. It is available in several molecular weights and hydrolysis grades [13]. The polymer has already showed its potency in formulating contact lens, articular cartilage, artificial muscle and vascular cell culturing hydrogel [14-15]. Very few literatures compare property differences among various PVAs under different conditions [16]. We have found huge difference in physical and mechanical properties in PVA-HPG blends where high molecular weight grade PVA (PVA_H, Mn 115k) and its oligomeric grade (PVA_L, Mn 14k) are used. The present article features some unique behaviors of these two PVAs, blended with HPG under low dose (5kGy) electron beam irradiation for different application. HPG is a familiar natural polymer used as thickener, stabilizer, etc. in several food items [17-18]. Low dose irradiation was used because it prevents excessive chain degradation and also promotes crosslinking in polymers [19].

There have been many literatures which discuss the effect of different nanomaterials into polymer matrix [20-21]. Generally, the nanoparticles enhance the physico-mechanical properties of the matrix subject to their size, shape, and concentration. Such as addition of anisotropic clay in PVA have increased mechanical and thermal properties [20]. Similarlyisotropic nano titanium dioxide (TiO_2) has improved thermal and mechanical properties of PVA and became suitable for direct methanol fuel cell application [22]. The present article compares effect of ex-situ MWCNT on dry- and wet-stage physical and mechanical properties between various PVA-HPG/MWCNT membranes. MWCNT is very important nanofiller which have been used mainly to improve thermal, mechanical and electrical conductivities in various polymer composite [23-24].To the best of our knowledge, not many studies have been carried out with ex-situ MWCNT/PVA-HPG composite membranes using different PVAs.

2. Research Method

2.1. Materials

High hydrolyzedgrade PVA (98% hydrolyzed) of widely different number average molecular weights 115k and 14k (designated as PVA_H and PVA_L)with narrow molecular weight distribution (PDI= 1.42) were purchased from Loba Chem, Mumbai, India. HPG was a gift sample received from Hindustan Gum. Haryana, India.N-Cetyl-N,N,N-Trimethyl ammonium bromide (CTAB) was purchased from HIMEDIA, Mumbai, India. MWCNT with outer diameter 8-15 nm, inner diameter 3-5 nm and length 10-50 µm was generously supplied by Cheap Tubes Inc., Brattleboro, USA.

2.2. Membrane preparation

At firs HPG and PVA were mixed in 1:10 weight proportion. Then the required solution was prepared by dissolving PVA-HPG mixture in hot distilled water under vigorous stirring. Next the formulated aqueous gel was placed into polyethylene bags with thickness of 5 mm and was irradiated at 5 kGy dose under high energy electron beam. The parameters of the accelerator were: electron energy 1.45 MeV; electron beam current 4mA; scanner width 90 cm and conveyor speed 3.6m min^{-1}. Then MWCNT premixed with 1% CTAB were added with post irradiated gel in different proportion under stirring and finally sonicated for 1 hour. Finally the gels were cast on plane Teflon sheets for spontaneous drying at room temperature. The average thickness of the membranes was maintained at 0.25 cm during casting. Detail of sample composition has been reported in Table 1.

2.3. Swelling and de-swelling kinetics study

Swelling of hydrogel membranes was done after putting membranes of uniform dimension ($5x2x0.25\ cm^3$) in distilled water at room temperature (27 ± 2^0 C). After stipulated time interval, the samples were taken out of the water, gently wiped in tissue paper to soak surface water and then weighed in an electronic balance (MK-20E, readability 0.1 mg, Adair Dutt, India). The swelling ratio was calculated by dividing swelled weight (S) by dry weight (S_0) of the hydrogel. The experiment was carried out till the samples attained equilibrium. Care was taken to avoid partial sample loss due to dissolution.

De-swelling experiment was done by periodically recording the decreasing weight of the fully swollen gel films in ambient air (27^0 C, RH: 85) till constant value.

Table1. Sample composition

Sample designation	PVA (w/v)	HPG (w/v)	MWCNT (%) (w.r.t., PVA)	Sample designation	PVA (w/v)	HPG (w/v)	MWCNT (%) (w.r.t., PVA)
PVA_H	10	0	0	PVA_L	10	0	0
PVA_H/HPG	10	1	0	PVA_L/HPG	10	1	0
PVA_H/HPG/0.2	10	1	0.2	PVA_L/HPG /0.2	10	1	0.2
PVA_H/HPG/0.5	10	1	0.5	PVA_L/HPG /0.5	10	1	0.5
PVA_H/HPG/1	10	1	1	PVA_L/HPG /1	10	1	1
PVA_H/HPG/2	10	1	2	PVA_L/HPG /2	10	1	2

2.4. Morphology study

Morphology analysis of composites was accomplished using a scanning electron microscope (SEM) procured from Zeiss, (EVO-MA10). The SEM was operated at 15kv during imaging. The images were taken by using cyroscopic technique after freezing the swelled hydrogel at the temperature of liquid hydrogen.

2.5. Mechanical properties study

Tensile stress-strain properties of the dry and fully swollen hydrogels were studied in a Lloyd UTM, USA. All the experiments were carried out at room temperature (27 ± 2^0 C) with these hydrogel membranes cut as per dimension of ASTM Die C and were pulled at a rate of 10 mm/min. An average of five test results has been reported for analysis.

2.6. Thermal Study

Thermal study from 30 ^oC to 550^oC was tested in a thermo gravimetric analyzer (TGA) (Perkin-Elmer, model No. 850), using a heating rate of 10^oC/min.

3. Results and Analysis

3.1. Swelling De-swelling analysis

Swelling kinetics of high and low molecular weight PVA-HPG/MWCNT hybrid membranes were continued till equilibrium was reached and results are plotted in Table 2. Pure PVA_H-HPG swelled at a faster rate as compared to pure PVA_L-HPG and finally equilibrates within much shorter time interval. PVA_L-HPG swells slowly than PVA_H due to higher amount of hydroxyl group present in PVA_H attracting water molecules faster than it [16]. The results indicate that overall swelling behavior of hybrid membranes have been affected in presence of MWCNT. In PVA_L-HPG series it is interestingly observed that net swelling ratios of PVA_L/HPG/0.5 are close to PVA_L/HPG. Improved swelling behaviour of PVA_L/HPG/0.5 is due to uniform dispersion of MWCNT which befitted in the available free volume of PVA_L/HPG matrix. Conversely, the swelling ratio decreases for membranes at higher MWCNT concentration (1-2wt%) in both series. At relatively higher MWCNT concentrations, the particles aggregate into larger domains. These hydrophobic domains bulge out of the surface and restrict diffusion of water molecules inside the membranes. Deswelling kinetics of hybrid membranes show that membranes absorbing higher amount of water also release it at faster rate due to high internal pressure gradient with the environment.

Table2. Swelling-de-swelling ratio

Sample	Swelling ratio							De-swelling ratio							
	30 sec	1 min	2 min	4 min	8 min	16 min	60 min	15 min	30 min	45 min	60 min	90 min	120 min	150 min
PVA_H-HPG	3.11	5.22	6.21	6.43	6.51	6.61	6.72	6.05	5.26	4.72	4.35	3.74	3.12	2.81
PVA_H-HPG/0.2	1.38	1.56	2.15	3.16	3.98	4.45	4.53	3.99	3.88	3.73	3.38	3.15	2.95	2.85
PVA_H-HPG/0.5	1.34	1.49	2.22	2.93	3.59	3.78	3.89	3.58	3.44	3.37	3.28	3.16	3.11	2.83
PVA_H-HPG/1	1.31	1.47	1.93	2.71	3.44	3.59	3.72	3.41	3.33	3.27	3.19	3.13	2.99	2.86
PVA_H-HPG/2	1.26	1.37	1.67	2.44	2.87	3.17	3.45	3.13	3.03	2.96	2.93	2.90	2.86	2.84
PVA_L-HPG	2.13	3.24	4.17	4.98	5.71	6.21	6.42	5.89	5.23	4.75	4.33	3.85	3.25	2.82
PVA_L-HPG/0.2	1.52	2.09	3.01	3.36	3.84	3.99	4.46	5.73	5.22	4.65	4.36	3.78	3.14	2.73
PVA_L-HPG/0.5	1.32	1.46	1.82	2.51	2.99	3.21	3.66	3.79	3.54	3.42	3.33	3.11	2.99	2.84
PVA_L-HPG/1	1.27	1.39	1.72	2.31	2.72	3.02	3.34	3.42	3.31	3.22	3.13	3.06	2.97	2.83
PVA_L-HPG/2	1.25	1.13	1.45	1.97	2.34	2.66	2.99	2.88	2.87	2.86	2.86	2.85	2.84	2.82

3.2. SEM image analysis

SEM images of the nanocomposites are shown in Fig. 1. PVA_H-HPG/1 showed the presence of “bundle” like structure of MWCNT with a thickness of 350 nm. This indicates poor matrix-filler interaction between MWCNT and PVA_L-HPG as individual MWCNT had a thickness of 15 nm. Again PVA_L-HPG/0.5 displayed the presence of finer network of MWCNT of average thichness of 80 nm which is relatively close to the thickness of individual MWCNT and indicates better matrix-filler interaction and higher crystalline packing due to better phase mixing between PVA_L-HPG and MWCNT. As low hydroxyl content and high hydrodynamic volume of PVA_L only permits lower MWCNT to enter into its smaller cavity.

3.3. Mechanical property analysis Fig. 2 demonstratesmechanical properties of various PVA-HPG/MWCNT hybrid membranes at different MWCNT concentrations in dry and swelled states. Tensile strength of dry PVA_H-HPG hybrid membranes increases up to 1 wt% MWCNT content while it is up to 0.5 wt% in case of PVA_L and thereafter decreases to lower value. Interestingly, PVA_L-HPG membranes exhibit more tensile strength and modulus than PVA_H-HPG membranes due to uniform MWCNT distribution and consequent rise in crystallinity. Drop in tensile strength and moduli demonstrate deleterious effects of large MWCNT aggregates which decreases PVA-HPG/MWCNT interaction beyond 1/2 wt%. The closely adhered MWCNT particles at low concentration assisted for dissipating the impressed mechanical stress on the membranes which, at higher MWCNT concentration, has failed since the bigger MWCNT aggregates act as stress concentrators. But in swelled state tensile strength increases upto 2 wt% and 1 wt% for PVA_H and PVA_L membranes respectively. This may be due to expansion of matrix cavity on swelling which permits more amount of MWCNT into it. Also elongation at break rises to a greater extent in the swelled state since accumulated stress released quickly in presence of excess water.

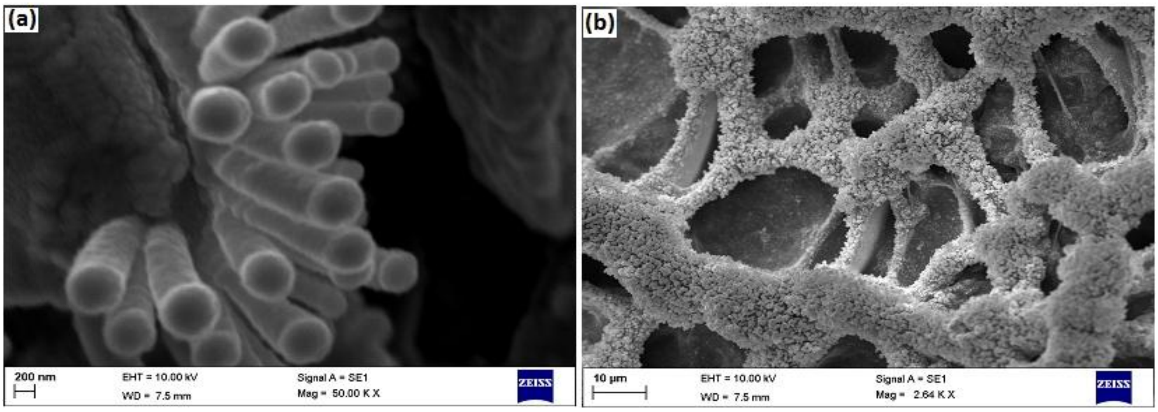

Figure 1. SEM images of (a) PVA$_H$-HPG/1 and PVA$_L$-HPG/0.5 membrane

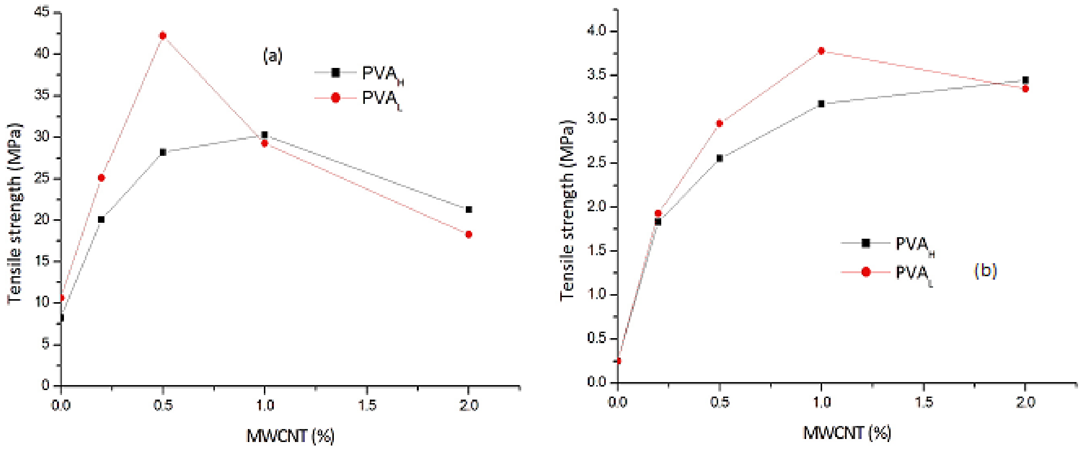

Figure 2. Mechanical property of (a) PVA$_H$-HPG and (b) PVA$_L$-HPG membranes.

3.4. Thermal analysis

Figure 3 shows thermogravimetry (TG) profiles of representative PVA$_H$-HPG/1 and PVA$_L$-HPG/0.5 composite membranes as they show best physico-mechanical properties in PVA$_H$ and PVA$_L$ series respectively. Both PVAs-HPG have shown two-step degradation- the first step, starting at 256^{0}C and completing at 370 ^{0}C, denotes side chain loss of PVA and decomposition of HPG [18,25] and the second step, starting at 458^{0}C and completing within 492^{0}C, denotes main chain loss. It is interesting to note that degradation profile altered on MWCNT addition (Figure 3a and b) i.e., onset of degradation was greatly delayed in both case as compared to PVA$_H$ and PVA$_L$.It is due to stronger interfacial interaction between PVA-HPG and MWCNT catalyzes more efficient heat transfer into MWCNT entities and delayed the degradation losses and stability of the composite membrane increases.

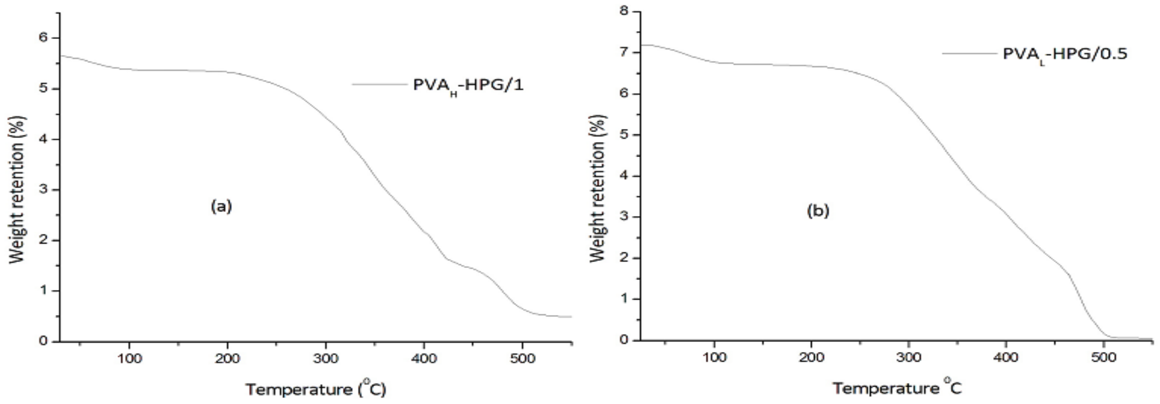

Figure 3. TG profile of (a) PVA$_H$-HPG/1 and (b) PVA$_L$-HPG/0.5 membranes.

4. Conclusions

High viscosity of HPG increases better crystallinity in PVA_L than PVA_H due to greater cohesive interaction between them. Low concentration of MWCNT in both cases produces better physico-mechanical properties because of finer dispersion of MWCNT into the matrix. At high concentration, the difference vanishes since cohesive interaction among MWCNT molecules becomes dominant and the best result was obtain for PVA_L/HPG/0.5 due to its superior property enhancement in all cases.

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