Synthesis and Study the Effect of HNTs on PVA/Chitosan Composite Material

Malek Ali

***Abstract*—**Composites materials of Poly (vinyl alcohol) (PVA)/Chitosan (CS) have been synthesized and characterized successfully. HNTs have been added to composites to enhance the mechanical and degradation properties by hydrogen bonding interactions, compatibility, and chemical crosslink between HNTs and PVA. PVA/CS/HNTs composites prepared with different concentration ratio. SEM micrographs of composites surface showed that more agglomeration with more chitosan ratio. Mechanical and degradation properties were characterized and the result indicates that Mechanical and degradation of 80%PVA/5%Chitosan/15%HNTs higher than the others PVA/CS/HNTs composites.

***Keywords*—**PVA/Chitosan, Composites, PVA/CS/HNTs, HNTs.

I. Introduction

DEVELOPING of biodegradable plastic materials is required by using natural sources such as starch, cellulose, chitosan. Chitosan is obtained from the deacetylation of chitin which is found in marine environments. Chitosan is insoluble in water, dissolved in acidic solutions before being incorporated into biodegradable polymer films [1], [2]. Chitosan has been used in very wide range of applications such as prevention of water pollution by chelating heavy metals, membrane separation in medicine and biotechnology, and in food packaging material [3], [4]. PVA has found also in many applications in pharmaceuticals, cosmetics and in the paper and food industries, either alone or in blends with other polymers such as poly (3-hydroxy butyrate) [5]. Poly(vinyl) alcohol/chitosan blends have attracted more attention as a biodegradable polymer blends due to their excellent biocompatibility and suitable physical properties, which can be used in environmentally friendly materials such as packaging, membrane filtration, dye adsorption and biomedical materials for controlled release, improved comfort, reduced irritation, and tissue engineering [6]-[9]. The miscibility between chitosan and PVA in the blend has been shown to depend on the preparation processing and the relative content of CS and PVA components. sorbitol employed as a possible candidate to modify the basic interaction between PVA and CS [10]. Few researchers have been studied the effects ratios of HNTs, and chitosan on the mechanical properties and biodegradable [11]-[13]. Therefore, in this study, poly (vinyl alcohol) has been selected to blend with chitosan and HNTs to study in details the effects of chitosan and HNTs ratios on the mechanical properties and biodegradable characterization of polymer.

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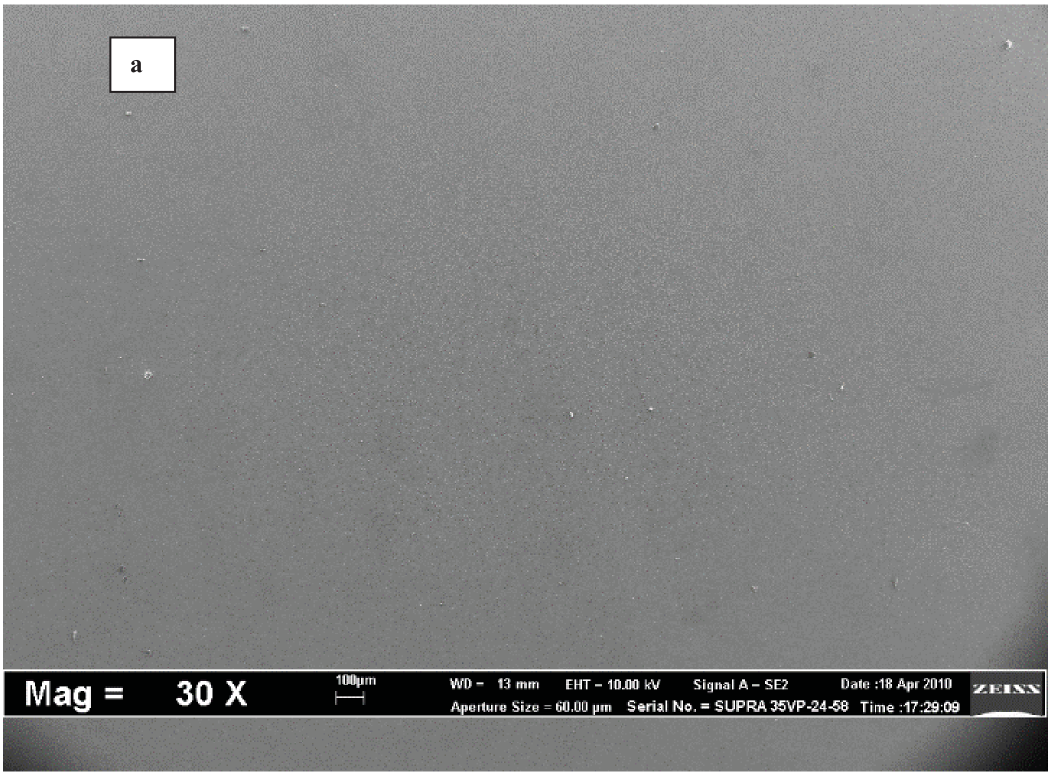
II. Experimental

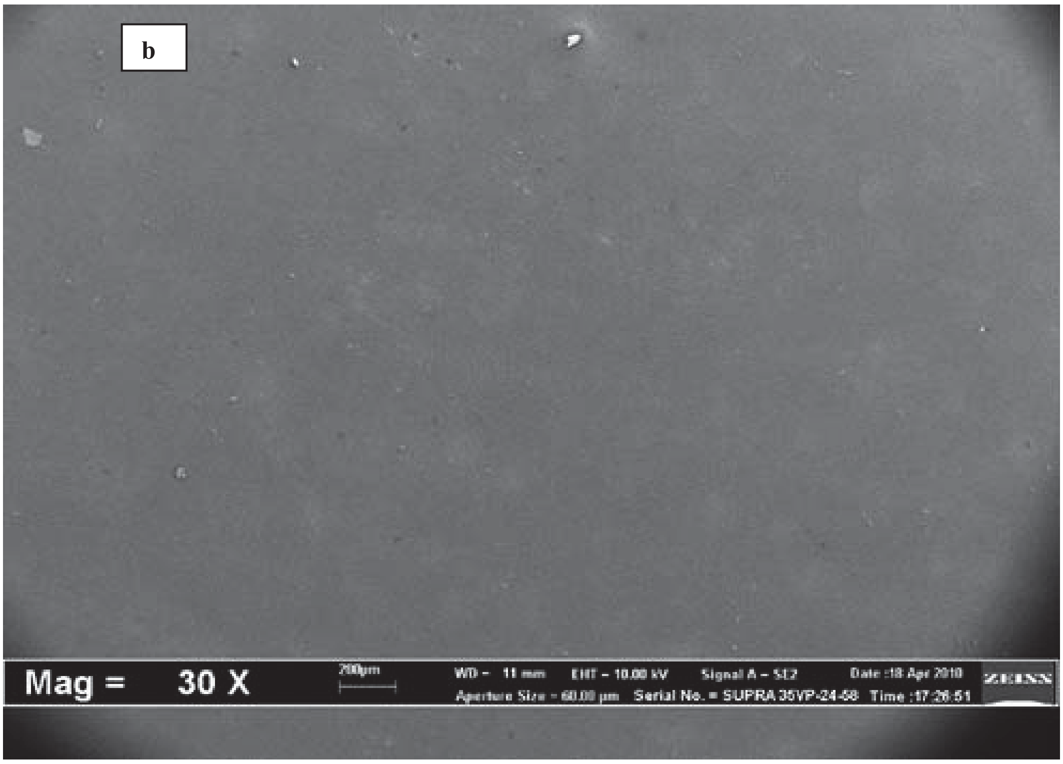
In the present study, the starting materials chosen were Poly (vinyl alcohol), PVA powder (hydrolysis MW=89,000-98,000, Tm = 126 ◦C and density 1.4406 g/cm3) was purchased from Sigma –Aldrich 99+ product of USA. Chitosan is obtained from the deacetylation of chitin and can be extracted from shellfish such as shrimp, lobster and crabs. powder (density= 1.54483 g/cm3) was purchased from Mega Makmur (M) Sdn, Bhd. Acetic acid R-COOH (purity = 99.98, density = 1.05 g/cm3 with MW 60 g mol-1) was purchased from merck-Germany (catalog no. 10063). Halloysite is a 1:1 aluminosilicate clay mineral with the empirical formula Al2Si2O5 (OH) 4. Its main constituents are aluminum (20.90%), silicon (21.76%), and hydrogen (1.56%). HNTs were purchased from Imerys Tableware Asia limited, New Zealand. halloysite nanotubes (HNTs) was added to PVA/chitosan solution after blending of PVA and chitosan solution as filler to enhance the mechanical properties. PVA grains were fully dissolved in 50 ml water by stirring at 95 °C for about 40 minutes. HNTs were dried for 8 h at 80°C and then dispersed in 20 ml water for 2h by ultrasonic treatment. Then, the nanosuspensions of PVA/HNTs were prepared by mixing the two stock solutions together and ultrasonic treatment for 2h. The chitosan was prepared by the same method mentioned before and then was added to PVA/HNTs solution and stirring for 2h by using 1500 rpm and then casting to the glass-dish. The films with (80% PVA / 15% CS / 5% HNT), (80% PVA / 10% CS / 10% HNTs), (80% PVA / 5% CS / 15% HNTs) and (80% PVA / 20% HNTs) respectively were prepared. The composites were assessed using tensile testing to determine the tensile stress, modulus of elasticity. Morphology of composites was analyzed by using SEM.

III. Results and Discussions

A. SEM Observations

HNTs added to composite to enhance the mechanical properties of the PVA/chitosan composite where the PVA/HNTs shows high compatibility especially blending with aid of ultra-sonic waves which offer many advantages. The selections of concentration of PVA/CS/HNTs are to show the effect of HNTs on the mechanical properties at higher PVA ratio where the immiscibility between PVA and CS. An ultrasonic mixer offers non-mechanical mixing which created homogenous mixtures of fine powders in a polymer melt and less wear from abrasion should occur, since there would be no mixing components directly in contact with the powder/polymer mix. Fig. 1 (a) shows that the blend of PVA/HNTs is completely compatible while Fig. 1 (b) shows less compatibility with presence of chitosan as a result of immiscibility of chitosan with PVA at high ratio. More agglomeration of chitosan has been noticed in Figs. 1 (c) and (d). The films were easy to remove form glass dishes but the thickness was to a range of 0.1-0.196mm. preprints.





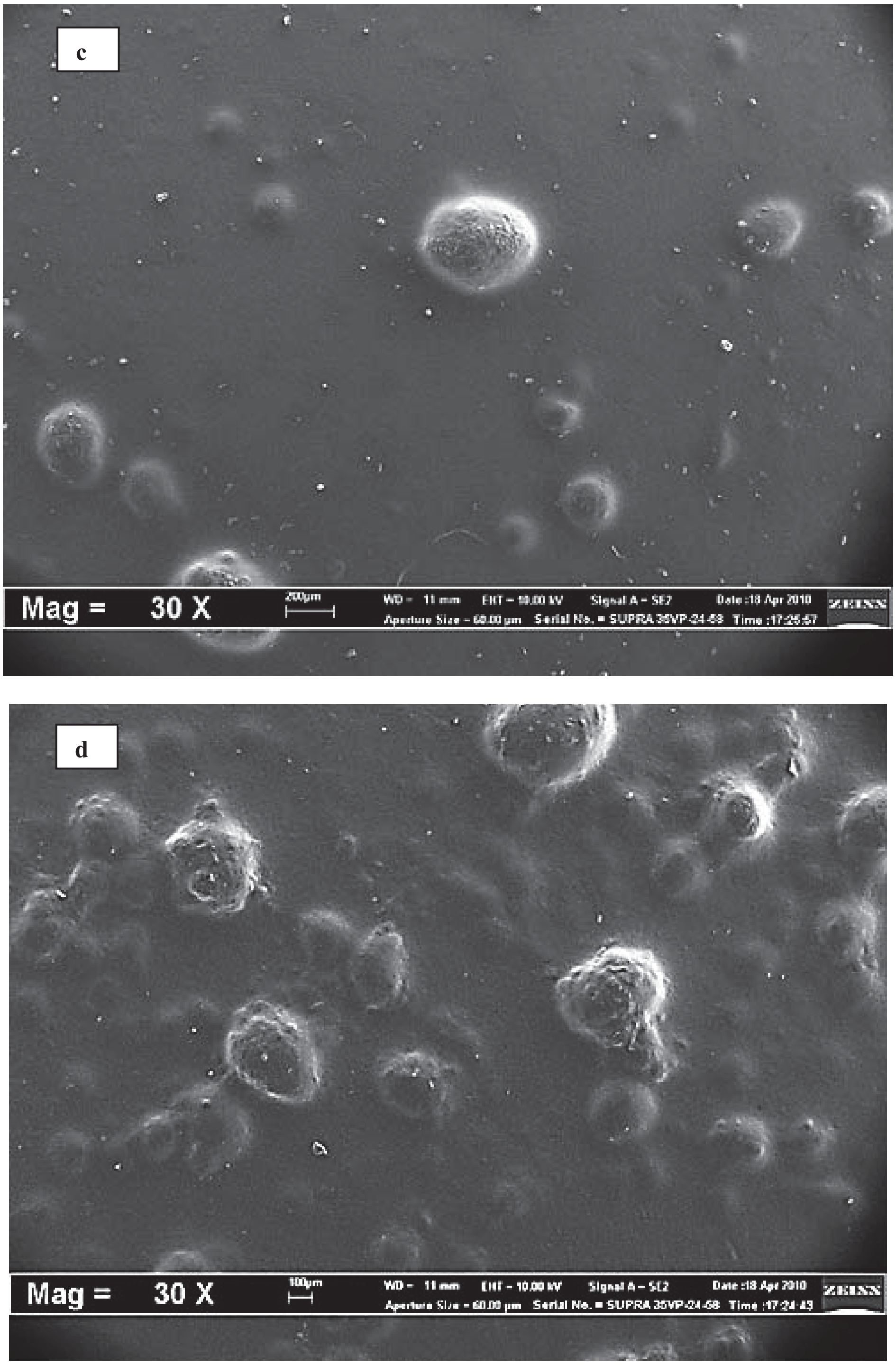


Fig. 1 SEM for different PVA / CS/ HNTs composites (a) 80%PVA and 20% HNTs, (b) 80% PVA / 5% CS / 15% HNTs, (c) 80%PVA / 10% CS / 10% HNTs, and (d) 80%PVA / 15% CS / 5% HNTs

B. Mechanical Degradability Properties

HNTs are a kind of aluminosilicate [$Al_2Si_2O_5(OH)_4 \times nH_2O$] clay with hollow nanotubular structure mined from natural deposits. Alumina and silica groups are located on the surfaces of HNTs especially on their crystal edges. The hydrogen bonding interactions between HNTs and PVA may make HNTs as an ideal candidate for PVA bionanocomposite film. The morphology of PVA/ HNTs film is relatively dense. HNTs have a good material compatibility with the PVA matrix via hydrogen bonding and the chemical crosslink between the HNTs and PVA. The mechanical properties have been improved by adding HNTs to the PVA/chitosan composites as shown in Fig. 2.

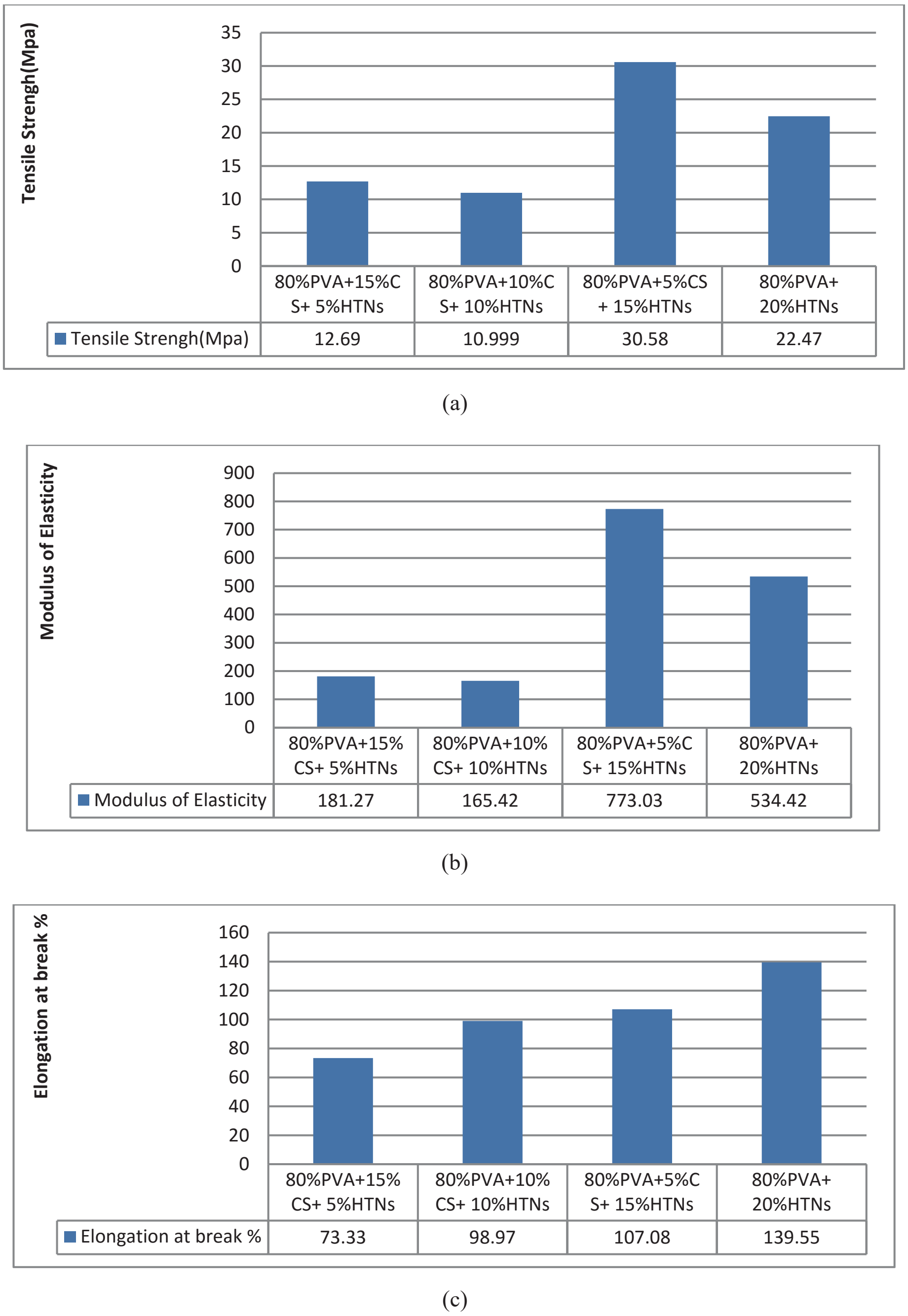


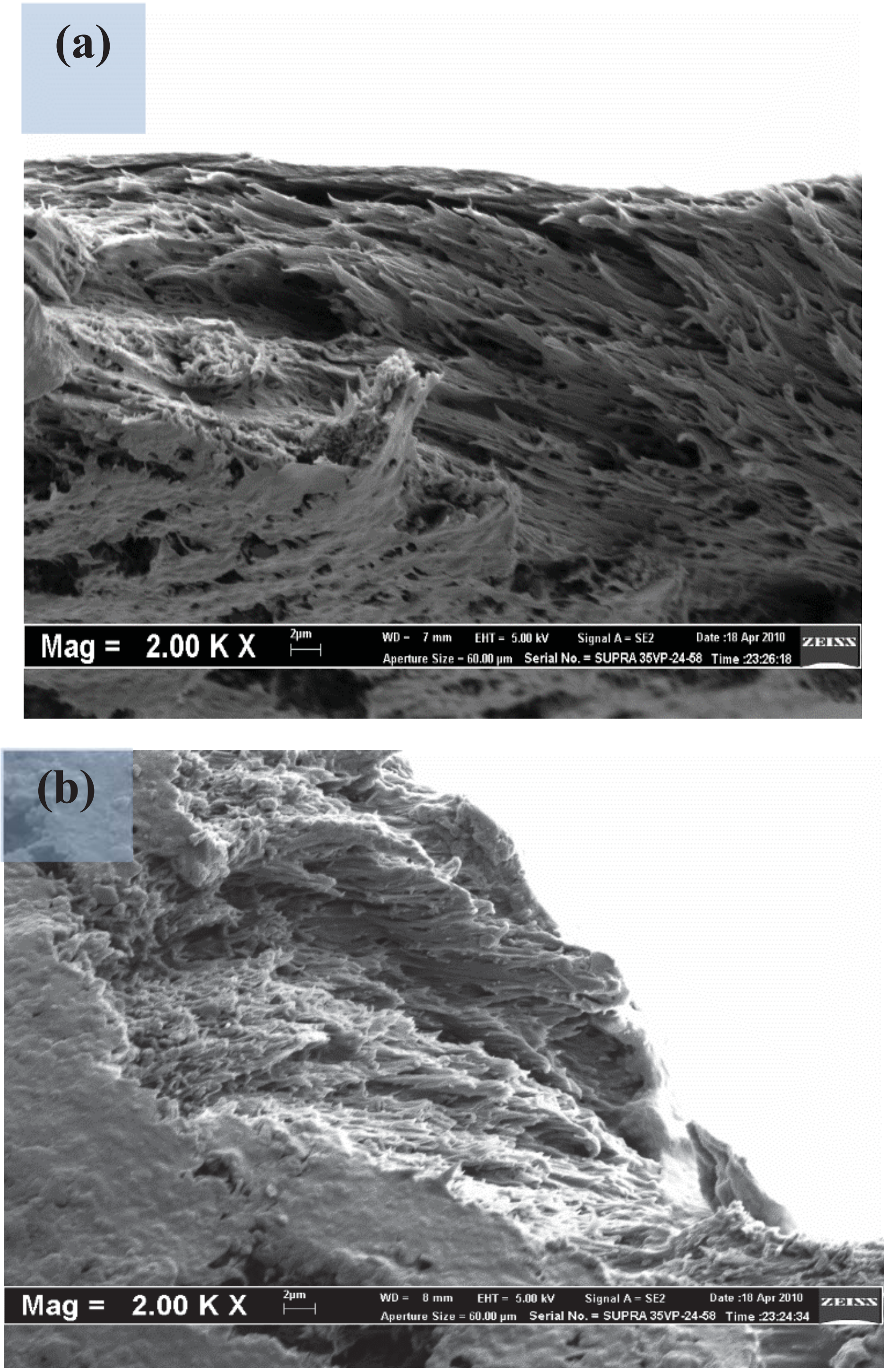
Fig. 2 (a) Tensile Strength, (b) Modulus of Elasticity, (c) Elongation at break for PVA/ with different ratio of Chitosan and HNTs

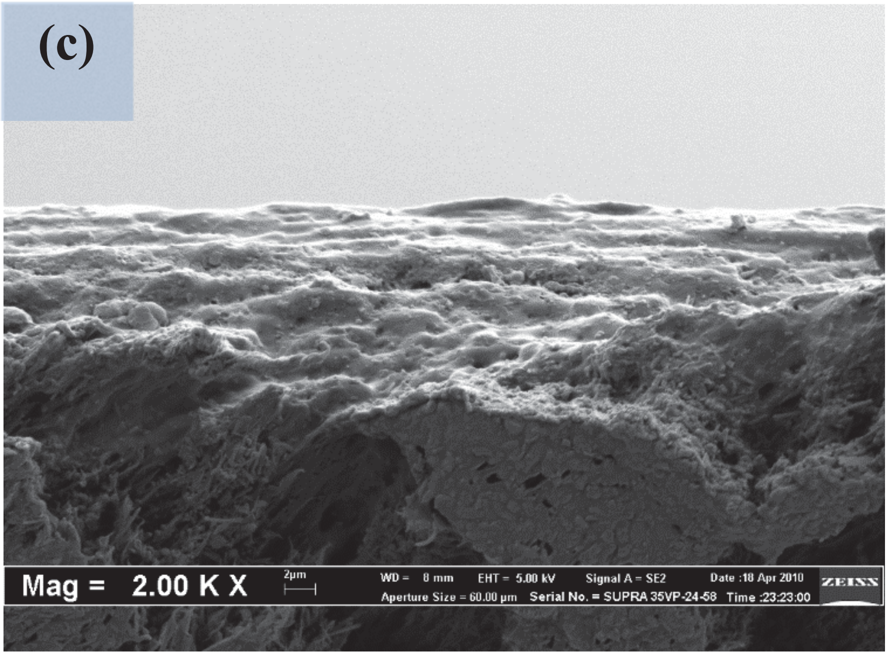
Tensile strength was increased by adding HNTs to PVA / chitosan composite, where it has been noticed that tensile strength of 80%PVA / 20%HNTs and 80%PVA / 5%Chitosan / 15%HNTs composites are more than the composites with higher chitosan ratio which belong to immiscibility between PVA and chitosan at high PVA ratio as well as it has been noticed that the composite with chitosan, 80%PVA / 5%Chitosan / 15%HNTs, has the maximum tensile strength where we can concluded that the composite with chitosan as well as HNTs improved the mechanical properties but due to immiscibility issue the mechanical properties have been decreased. The same thing was observed with elastic modulus while it has been noticed that the elongation at break have been increased with increasing of HNTs. By comparing the same chitosan ratio without HNTs and then with presence of HNTs we can find that the HNTs enhance the mechanical properties more than before and we can clearly notice.

C. Fracture Surfaces Cross-Section of the Samples

Tensile fracture patterns are different in Figs. 3 (a)-(d) where in (a) a good dispersion of HNTs was obtained and no aggregate or obvious cavities can be found also most of HNTs are uniformly dispersed in PVA matrix. Ductile deformation still exists in sample 80%PVA, 5%chitosan and 15%HNTs as shown in Fig. 3 (b) but the elongation/stretched of the sample was lower due to presence of chitosan where the ductile fracture tend to be brittle with more chitosan ratio as in Figs. 3 (c) and (d) where in (d) it is clearly that the sample was not stretch or elongate before failure, brittle fracture, of the sample. The propagation of a ductile crack involves substantial plastic flow and ductile fracture usually gives a characteristic rough fracture surface. Fracture occurs by a process known as microvoid coalescence.

Halloysite is very sensitive to water and its solubility in water is very high which lead to loss the structure rapidly. (80%PVA / 20%HNTs and 80%PVA / 5%chitosan / 15%HNTS) have been failed within first two minutes while the film (80%PVA / 10%chitosan / 10%HNTs) have been failed within 15 minutes.





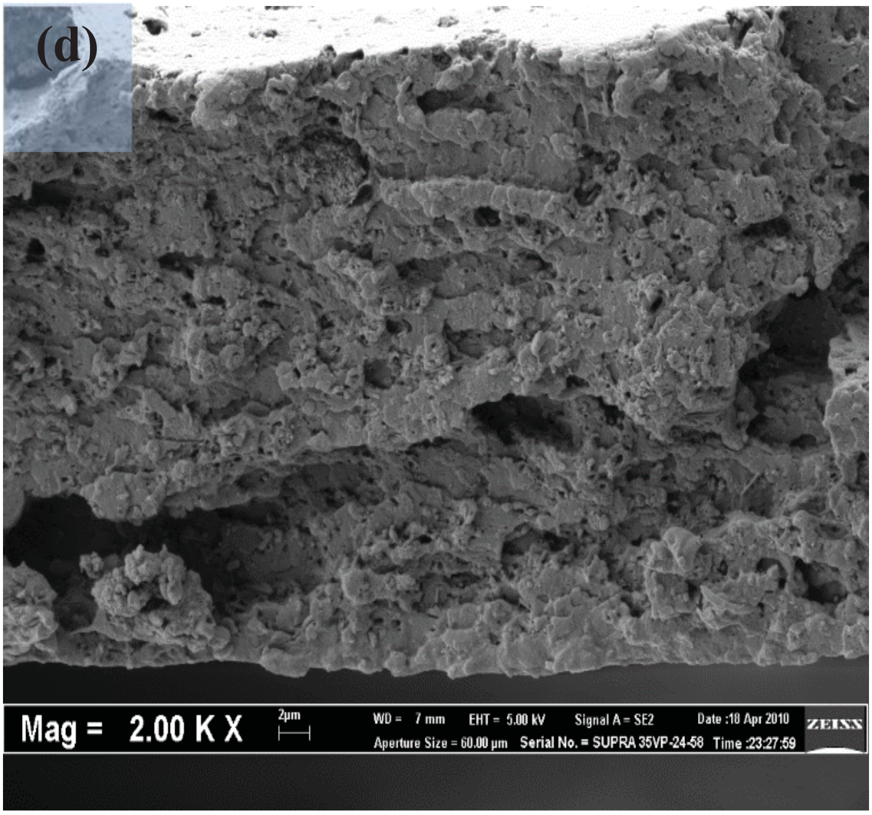


Fig. 3 SEM micrographs for the fracture surface of different PVA / CS / HNTs composites (a) 80%PVA and 20% HNTs, (b) 80% PVA / 5% CS / 15% HNTs, (c) 80%PVA / 10% CS / 10% HNTs, (d) 80%PVA / 15% CS / 5% HNTs

IV. Conclusions

PVA/CS/HNTs composites have been prepared with different concentration ratio. HNTs have been added to composites to enhance the mechanical and degradation properties. SEM micrographs of composites surface showed that more agglomeration with more chitosan ratio. The result indicates that Mechanical and degradation of 80%PVA/5%Chitosan/15%HNTs higher than the others PVA/CS/HNTs composites. The morphology of PVA/ HNTs film is relatively dense. In all PVA/CS/HNTs composites HNTs have uniformly dispersed in PVA matrix.

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