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Functionalized Multi-Walled Carbon Nanotubes and Micro Cellulose Reinforced Poly (Vinyl Alcohol) Hybrid Composite Films: Characterization and Reprocessing Performance

Araştırma Makalesi / Research Article

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ABSTRACT

The aim of this research paper was to investigate the synergetic effect of micro cellulose and multi-walled carbon nanotubes (MWCNTs) combination on physicochemical, mechanical and reprocessing performance of Poly (Vinyl Alcohol) hybrid composite films. The hybrid composite films production was carried out by the solution casting method, and the reprocessed films were produced using defective (torn, faulty) films from primary production by the same method. The combined use of MWCNTs and micro cellulose improved the hydrophobicity approximately 85% in ratio. After the reprocessing, decreased intensities of the peaks in the FTIR and Raman results confirmed the reduced molecular interaction between all components of the hybrid composite film, moreover, SEM and TEM revealed the negative defects such as agglomeration which caused mechanical strength decrease. The tensile strength of PVA hybrid composite films loaded cellulose/MWCNTs, reached 97 MPa strength value and elongation at break decreased to 33% according to the neat PVA film. The study results revealed that hybridization had a remarkable impact on improving characteristic properties of composite films and reprocessing process might have been compatible with solution casting method.

Keywords: Multi-walled carbon nanotubes, micro cellulose, PVA, hybrid, composite film.

Fonksiyonel Çok Duvarlı Karbon Nanotüp ve Mikro Selüloz Takviyeli Poli (Vinil Alkol) Hibrit Kompozit Filmler: Karaterizasyonu ve Yeniden İşlenme Performansı

ÖZ

Bu araştırma çalışmasının amacı, mikro selüloz ve çok duvarlı karbon nanotüp (MWCNTs) kombinasyonunun, Poly (Vinyl Alcohol) hibrit kompozit filmlerin fizikokimyasal, mekanik ve yeniden işleme performansları üzerindeki sinerjik etkisini araştırmaktır. Hibrit kompozit filmlerin üretimi, çözelti döküm yöntemi ile gerçekleştirilmiş ve yeniden işlenmiş filmler, aynı yöntemle birincil üretimden kaynaklanan kusurlu (yırtık, hatalı) filmler kullanılarak üretilmiştir. MWCNT'lerin ve mikro selülozun birleşik kullanımı hidrofobikliği yaklaşık olarak% 85 oranında arttırdı. Yeniden işleme tabi tutulduktan sonra, FTIR ve Raman'daki tepe noktalarının azalan yoğunlukları, karma kompozit filmin tüm bileşenleri arasındaki azalmış moleküler etkileşimin, ayrıca SEM ve TEM'in mekanik mukavemet azalmasına neden olan topaklanma gibi negatif kusurları ortaya çıkardığını doğruladı. Selüloz / MWCNT takviyeli PVA hibrid kompozit filmlerin gerilme mukavemeti, 97 MPa kuvvet değerine ulaşmış ve kopma uzaması, saf PVA filmine göre% 33'e düşmüştür. Çalışma sonuçları, hibridizasyonun kompozit filmlerin karakteristik özelliklerini iyileştirme konusunda dikkate değer bir etkisi olduğunu ve yeniden işleme sürecinin çözelti döküm yöntemiyle uyumlu olabileceğini ortaya koydu.

Anahtar Kelimeler: Çok duvarlı karbon nanotüp, mikro selüloz, PVA, hibrit, kompozit film.

1. INTRODUCTION

In the last decades, nanotechnology is an engineering field which offers much use in the novel multifunctional materials with improved properties. In this context, the use of carbon nanotubes, a nanotechnology product with unique atomic and mechanical properties, has continued to be an attractive field of research. Even though nano-reinforcements offer attractive properties, they cannot meet all the needs of the composite structure they are embedded. There are some lacks about adhesion, load transfer or other major requirements between nano-reinforcement and large-scale matrix. If the advantages of nanotechnology and polymer matrix are brought together in a hybrid composition, they can eliminate the deficiencies of the new material [1–4].

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Poly (vinyl alcohol) (PVA) is a useful water-soluble, non-toxic, transparent synthetic polymer which has been widely studied and applied in the form of fiber, film, and gel [2,5–7]. PVA has a strong hydrophilic structure and hydrogen bonding character; thus, it is able to form thin-film or membrane [6,8]. However, PVA has poor mechanical performance which may restrict the PVA film in the heavy-duty applications. To remedy this deficiency, various reinforcement materials have been incorporated into PVA matrix to provide the necessary change in the physical and mechanical properties of PVA film and composites [5,9,10]. Synthetic multi-walled carbon nanotubes (MWCNTs), which exhibits superior physical and mechanical properties as well as cellulose derived from sustainable plant-based raw materials, is at the forefront in many reinforcing applications [4].

Considering the structural changes, it is well known that micro-nano combinations give superior mechanical properties to the polymer matrix due to their distribution, aspect ratio and orientation. The effect of micro-cellulose or multi-walled carbon nanotubes on the mechanical properties of PVA composites has been studied, previously. Incorporating of cellulose make the polymer matrix like PVA stronger and well-ordered internal structure and this structure exhibits good mechanical performance due to good load transfer mechanism. In studies examining the impact of the contribution of micro-cellulose, Tanpichai et al. [4] investigated micro-fibrillated cellulose reinforced PVA. They observed an increase in both the tensile strength and modulus of the composites was observed for up to 3 wt % fibril reinforcements. In addition, focusing on only the type of reinforcement makes it difficult to clearly understand the results represented in the final composite product. It worth noting that the production conditions also impact the final product structure from the molecular level to the macro properties. Peng et al. [11] reported an improvement in tensile properties (i.e., ultimate strength and elastic modulus) which depended on short cellulose nanofibrils loading, PVA crystal orientation and draw ratio (hot drawn) in their study. Overcoming problems such as homogeneous dispersion or agglomeration in processes using nanoscale reinforcements cause significant changes in the whole composite structure. Mallakpour et al. [5] reported that l-Phenylalanine amino acid functionalized MWCNTs showed better dispersion in water and improved mechanical and physical properties were also achieved on PVA composite film. The purpose of using hybrid composition in composite production is to reflect the interactions of the different characteristic reinforcements and their different responses to external loading in the composite structure, as improved properties to the whole structure. The research of Montes et al. [3] revealed that the use of cellulose nano-crystal-stabilized graphene improved the tensile strength and Young's modulus about 20% and 50%, respectively, compared with neat PVA. The overall research results still need in-depth data about composite structures consist of a hybrid combination such as micro cellulose and multi-walled carbon nanotubes.

This study reports an investigation about a hybrid composite film which includes nano and micro-sized reinforcements in its structure. Besides, another goal of this study was to expose the defective (torn, faulty) films (from the primary production) to the reprocessing with same parameters and to detect the molecular, physical and mechanical changes in the reprocessed hybrid composite films. The physical (hydrophily) and mechanical properties were determined by the means of contact angle measurement, UV-Visibility, and tensile test. The scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used to scan the morphology of composites. And the chemical structures of hybrid composite films were identified by an ATR-Fourier transform infrared spectroscopy (FTIR) and Raman spectroscopy.

2. MATERIAL and METHOD

2.1. Materials

Micro cellulose (Arbocel) was supplied from J. Rettenmaier & Söhne GmbH + CO Germany. The fiber length of approximately 90% of cellulose content is 50 µm, its fiber thickness is 35 µm, and bulk density is 70 g l-1. Multi-walled carbon nanotubes (MWCNTs, purity > 95 %) produced by chemical vapor deposition (CVD) were purchased from Joyful Grow (Shanghai, China). The inner diameter and outer diameter of MWCNTs are 3-5 nm and 8-15 nm, respectively. Length is 3-12 µm, density is 0.15 gr/cm^{-3}. Poly (vinyl alcohol) (PVA) was supplied from ADR Group, purity is 87.8% (CAS No:9002-89-5). Diiodomethane (reagent plus, 99%),

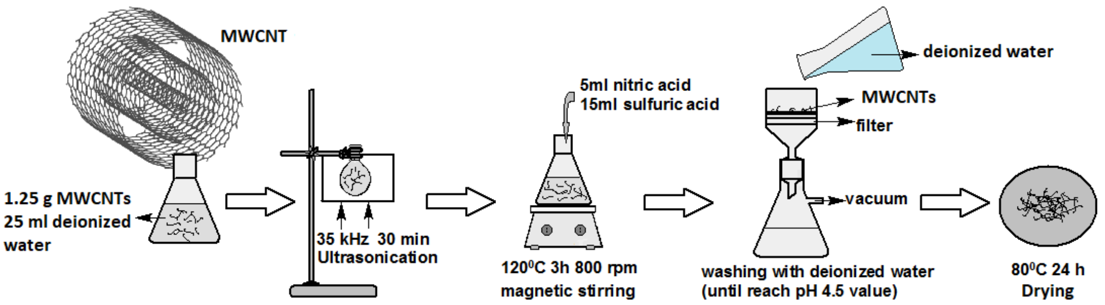


Figure 1. Carboxylation of MWCNTs

nitric acid (ACS reagent, 70%) and sulfuric acid (reagent grade, 95-98%) were purchased from Sigma (St. Louis, MO, USA). Deionized water obtained from a PURELAB® Option-Q (ELGA LabWater, UK) unit at a conductivity less than 0.5 µS cm^{-1}.

2.2. Carboxylation of MWCNTs

The carboxylation process was performed to introduce carboxyl groups onto the surface of the MWCNTs to increase the compatibility among components of the composite film according to the method reported by [11,12] with slight modifications. 1.25 grams of MWCNTs were dispersed in 25 ml distilled water for 30 min by using a Sonicator (35 kHz) (Sonorex super, Bandelin, Berlin, Germany). The 5 ml of HNO_3 and 15 ml H_2SO_4 was added into the resulting MWCNT dispersion at 120 °C and hold for approximately 3 h. After filtering the solid sample was washed repeatedly with deionized water until the filtrate pH value approached 4.5 and then dried in a vacuum oven (Nuve, EV018, Ankara, Turkey) at 80 °C for 24 h. After being oven-dried, the carboxylated MWCNTs (i.e., MWCNTs-COOH) were obtained and these carboxylated MWCNTs were denoted as functionalized-MWCNTs (f-MWCNTs). The carboxylation process of MWCNTs was given in Figure 1.

2.3. Preparation of f-MWCNTs/Micro Cellulose/PVA Composite

A 10 wt % aqueous solution of PVA powder was stirred at 90 ºC for 1 h by using magnetic hot stirrer (Mtops MS300HS, Korea) [13]. The neat PVA solution poured into a Petri dish to produce neat PVA film and the solution was dried for 7 days at room temperature (23 ± 2 °C). Then free-standing 60 µm thick films were peeled from the glass plate and were subjected to different tests.

In the production process of PVA-micro cellulose composite film, firstly, micro cellulose fibers (5 g) were soaked in deionized water (100 ml) for 24 h before use. And then, fibers were mixed for 1 h by using magnetic stirrer, after this step, they were sonicated using a high-intensity sonifier (35 kHz, 320 W) for 10 minutes [11]. During the ultrasonic process, the solution was cooled in an ice/water bath to avoid solution overheating. The solution was mixed with the neat PVA solution and stirred for 1h at 90 °C. After, the stirring solution was poured into a Petri dish. Drying process was completed in 7 days.

The f-MWCNTs were dispersed in deionized water through stirring for 3 h and sonicated for 30 min. [5]. Both PVA and f-MWCNTs solutions were mixed, stirred for 1 h at 90 °C, and again sonicated for 30 min. The mixture was poured into a petri dish to form composite films. The solution was dried for 7 days at room temperature (23 ± 2 °C).

The similar solution casting method was used to prepare the PVA, f-MWCNTs, micro cellulose composites. The prepared micro cellulose and f-MWCNTs solution were incorporated into neat PVA solution. After magnetic stirring 30 min and sonication 30 min, the solution was poured into a Petri dish. Drying process accomplished at 7 days. The process of composite preparation was shown in Figure 2 in detail.

Reprocessing was performed by using the similar procedure. Defective composite films were dissolved in deionized water at 90 °C. After 1h magnetic stirring and 30 min sonication, solution poured into Petri dish. The solution was dried for 7 days at room temperature (23 ± 2 ºC). All tests were repeated for the reprocessed samples. The sample codes of composite films were presented in Table 1.

Table 1. Prepared composite films and sample codes

Sample code	PVA wt.%	MWCNT wt.%	Cellulose wt.%
PVA	100	0	0
PVA/r	100	0	0
PCe	95	0	5
PNT	95	5	0
PCeNT	95	2.5	2.5
PCe/r	95	0	5
PNT/r	95	5	0
PCeNT/r	95	2.5	2.5

r:Reprocessed

2.4. Contact Angle and Surface Free Energy Measurements

The contact angles of composite films were measured with Theta Optical Tensiometer (KSV Attension Instruments, Helsinki, Finland) according to the sessile drop method technique using two different test liquids (ultrapure water and diiodomethane). The contact angle measurements were performed at 5 random locations on the composite film surfaces at room temperature (23 ± 2 ºC) and were expressed as the mean of these measurements and the standard deviation. The mean contact angle values were used to calculate the components of surface free energy (SFE) according to the Owens–Wendt method (1969) described by Huner, Gulec, Damar Huner [14] in detail.

2.5. Raman Spectroscopy

Raman spectroscopy was used to better understand the interfaces interaction between micro cellulose, MWCNTs and PVA. Raman spectra of the composite films were recorded using a DXR Raman Microscope (Thermo Fisher Scientific, Madison, Wisconsin) equipped with a laser source which has 532 nm excitation wavelength. Spectral resolution was 5.0 cm^{-1}. All the spectra were collected in the range 100–3500 cm^{-1}.

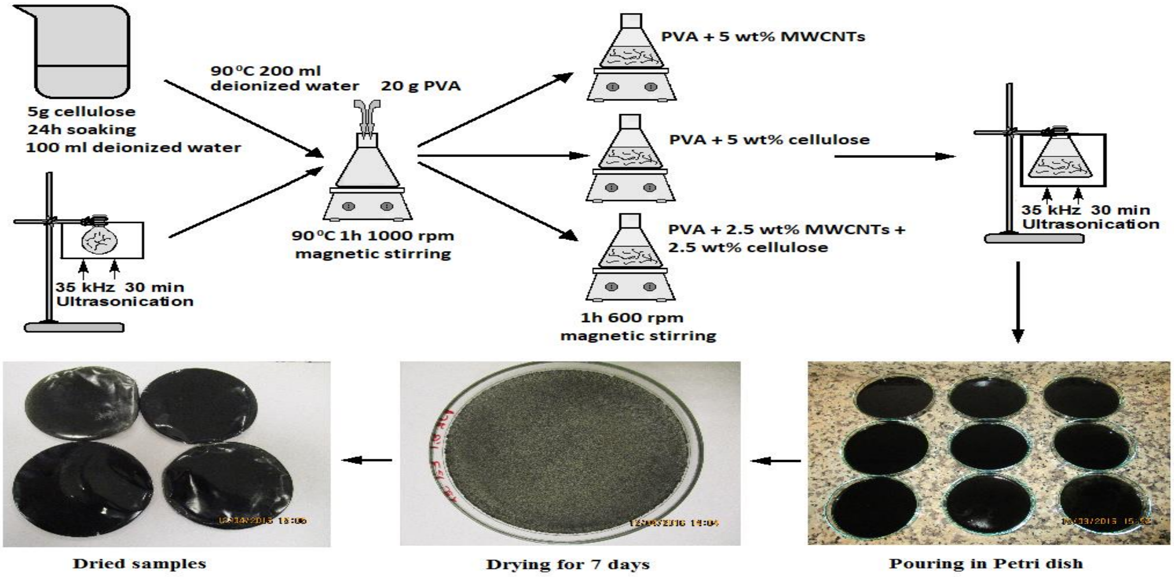


Figure 2. Composite preparation processes

2.6. Scanning Electron Microscopy (SEM)-Transmission Electron Microscopy (TEM)

The MWCNTs and micro cellulose structures were investigated by TEM. A few drops of diluted composite solution (0.5 wt % in water) were deposited on a TEM copper grid and dried. The sample grids were analyzed using a JEOL TEM-1400 (Jeol, USA) at an accelerating voltage of 120 kV.

The morphological characteristic of composite samples was carried out using a QUANTA FEG 250 (Oregon, USA) scanning electron microscope with LFD (wide area, low vacuum) detector. An accelerating voltage of 2 and 5 kV was used to collect the SEM images.

2.7. Attenuated Total Reflectance– Fourier transform infrared spectroscopy (ATR-FTIR)

ATR-FTIR spectroscopy was used to get information about the functional group that exists in PVA composite films. The IR spectra of the films were obtained using an IR spectrometer (Perkin-Elmer spectrum BX, Perkin-Elmer, Canada). ATR-FTIR spectra of the samples were collected in the range of 4000-400 cm^{-1} with a resolution of 4 cm^{-1}. Composite surfaces analyzed were in contact with a ZnSe crystal with a 45° angle of incidence. At least five samples were analyzed.

2.8. UV-visible spectroscopic analysis

The UV-vis spectra of the PVA and composite films were recorded using a UV-Vis spectrometer (UV-1800, Shimadzu, Kyoto, Japan) in the visible light wavelength region of 200–800 nm at 25 ºC. The absorbance spectra were acquired using air as background.

2.9. Mechanical testing

Specimens were prepared using a razor blade according to ISO 37-3 standard and tested at a crosshead speed of 50 mm min^{-1}. The dimensions of each specimen were 50 mm in length by 4 mm in width. The thickness of each specimen was measured by using Mitutoyo Digital Outside Micrometer (Kanagawa, Japan, ±0.001 mm repeatability). The average thickness of the films was measured randomly at five different locations on each film samples. Before the tensile test, all specimens were kept in a controlled room at 23 ± 2 ºC and 50 ± 2% relative humidity for 24 h. At least 5 samples were tested for each composite films.

3. RESULTS AND DISCUSSION

3.1. Contact angle results

The contact angle (CA) values of the neat PVA and the PVA composite films were listed in Table 2. PVA is a semi-crystal hydrophilic polymer consist of one hydroxyl group in each repeat unit and hence cross-linkable [15]. Therefore, the water droplet was absorbed by the neat PVA polymer very quickly [8]. In this case, the neat PVA showed about 38° CA value. After incorporation of micro cellulose or MWCNTs, CA value increased according to the neat PVA. Both micro cellulose and MWCNTs reinforcement provided maximum CA value.

Previous studies [5,9,10,16–18] revealed that chemical treatment, heat treatment, a cross-linking agent can make PVA structure more hydrophobic due to changing its crystallinity or cross-linking. Micro cellulose acted as a cross-linking agent in the PVA structure [11]. In the cross-linking with micro cellulose, polar groups (like –OH) of PVA matrix, take part in cross-linking reaction, and it prevents moving of polar groups to the surface of the polymer. On the other hand, the presence of MWCNTs affected the surface morphology of PVA matrix due to changing crystallinity of structure [19]. MWCNTs and the amorphous state of PVA surface formed more hydrophobic surface. After the

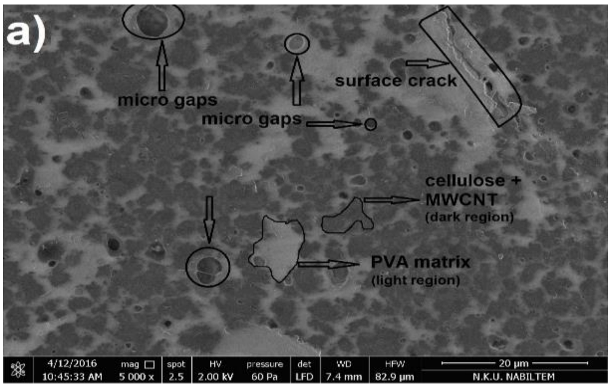
Table 2. Contact angle measurements of primary production and reprocessed composite films

	PCe	PNT	PCeNT	PCe/r	PNT/r	PCeNT/r
θ_W(°)	56.7±2.5	85.1±2.3	70.6±0.7	42.0±0.7	69.6±0.5	55.3±0.6
θ_D(°)	42.1±1.0	29.0±2.0	34.3±0.5	33.5±0.8	39.0±5.0	39.9±0.7
γ_s^d (mJ/m^2)	38.5±0.5	44.6±0.8	39.9±0.2	42.7±0.4	39.9±0.2	42.1±0.3
γ_s^p(mJ/m^2)	15.0±1.3	1.4±0.4	7.2±0.4	21.7±0.4	7.7±0.4	14.4±0.3
γ_s^{tot} (mJ/m^2)	53.5±1.8	46.0±1.2	47.1±0.4	64.4±0.5	47.6±0.4	56.5±0.4
$\gamma_s^p/\gamma_s^{tot}$	0.28	0.03	0.15	0.33	0.16	0.25

r:Reprocessed; γ_s^d: Disperse component; γ_s^p: Polar component; γ_s^{tot}: Surface total energy

hybridization process, PVA composite films exhibited more hydrophobic behavior due to both presence of micro cellulose and MWCNTs. Montes et al. [3] reported a decrease of PVA nucleation in the presence of cellulose nanocrystals. These interactions most probably restricted the capability of the matrix chains to form large crystalline domains. But the presence of the small amount of graphene in the PVA/ cellulose nanocrystal composite structure increased the degree of crystallinity [3,6,20]. Incorporation of MWCNTs into matrix demonstrated the same effect in this study. Consequently, it provided the increase of contact angles. Figure 3a) depicts MWCNTs and micro cellulose reinforced PVA surface.

The reprocessed composite film showed a decrease in contact angle values. It may be attributed to the reduction in molecular interaction between PVA matrix and reinforcements due to reprocessing. Surface total energy (γ_s^{tot}) almost did not change but polar component increased after reprocessing. As previously described, the increase of surface polar component causes the decrease of water contact angle value. And also, Figure 3b) revealed that surface roughness of composite film increased after reprocessing. Surface roughness affects the contact angle measurement, vigorously. Increased reinforcement ratio causes nonuniform surface structure. This can be explained agglomeration of reinforcements.



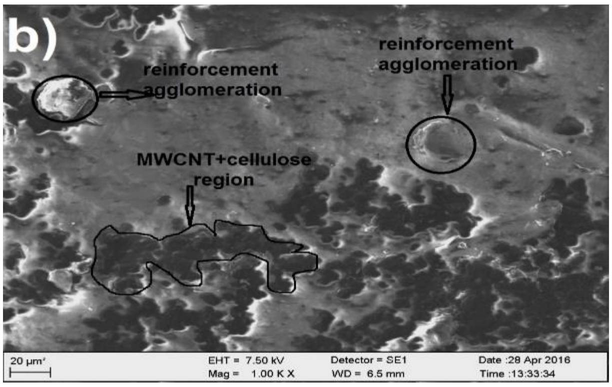


Figure 3. SEM micrograph of composite film surface a) 5% MWCNT and cellulose reinforced PVA surface b) agglomeration and reinforcement regions of PCeNT/r composite

3.2. Raman results

Raman spectroscopy was utilized to examine the interactions between the polymer and reinforcements. Figure 4a) shows Raman spectra of neat PVA and composites. Figure 4b) depicts Raman spectra of the reprocessed samples. The Raman spectrum of PVA showed a peak at 2921 cm^{-1} which is assigned to the intrinsic (CH_2) stretching band [1]. All micro cellulose containing composites showed a peak near 1095 cm^{-1} (D band) due to the presence of cellulose [4]. The Raman peak initially located at 1095 cm^{-1} corresponding to the C–O stretching. The band at 1245 cm^{-1} (G band) corresponds to C=C, sp2-hybridized carbon, derived from the MWCNTs structure [21]. And also, -COOH structure appeared at near 3050 cm^{-1} (G' band). This band indicates that there might be an interaction taking place in the form of hydrogen bonding between the carboxyl and hydroxyl groups of MWCNTs-COOH and PVA matrix [4].

Reprocessing effect on Raman spectra has been shown in Figure 4b). While micro cellulose effect disappeared remarkably, MWCNTs maintained the effect on composite structure, decreasingly. As shown in Figure 4b), at 1370 cm^{-1} (D band), a strong band appeared in the Raman spectra of MWCNTs which stem from the sp3-hybridized carbon or structural defects. Additionally, at

1550 cm^{-1} (G band), a relatively weak band corresponded to vibration of sp2-hybridized graphitic domains [4,21].

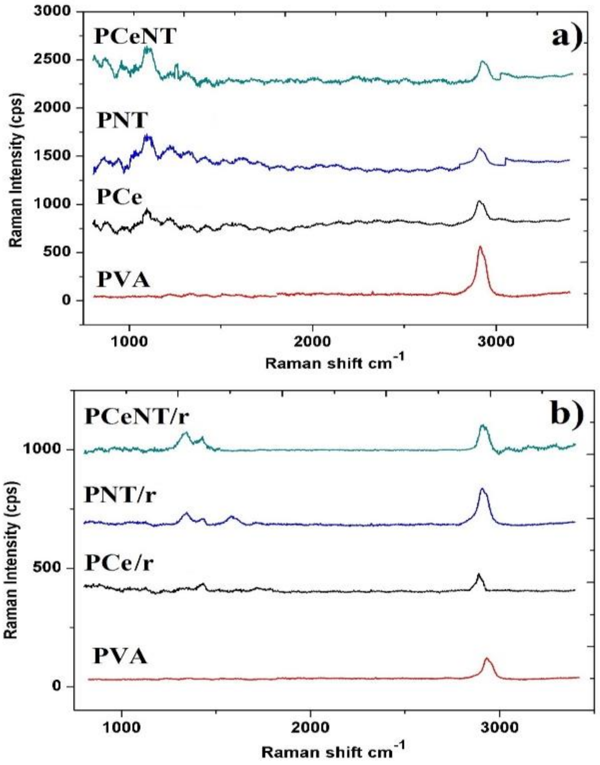


Figure 4. Raman spectra of PVA composite films a) primary production composite films b) reprocessed composite films

3.3. ATR-FTIR results

The interactions between MWCNTs, micro cellulose, hybrid composition, and PVA were observed by FTIR and the results are shown in Figure 5. An important absorption peak was verified at 1150 cm^{-1}, which is associated with the C–C stretching mode of PVA and is generally related to the crystallinity of PVA [9,20]. The absorption band at 1055 cm^{-1} in the spectra of micro cellulose fiber is attributed to the C–O stretching vibration and anomeric carbon b-D-glucopyranosyl of cellulose, indicating the typical structure of cellulose [11,22]. For the MWCNTs, the characteristic peaks in FTIR spectra represented at 1750 cm^{-1} and 1640 cm^{-1} indicated the stretching vibration of carboxylic acid C=O (Oswald-Lehman) and C=O amidic groups, respectively [5]. The presence of amidic group was represented as a proof of MWCNTs in the structure by Mallakpour et al. [5]. FTIR results of this case also revealed that increase of MWCNTs ratio did not significantly change the intensity of peak. This may be attributed to the presence of the structure of MWCNTs-COOH which bond with neither PVA nor micro cellulose. The large bands were observed between 3600 and 3200 cm^{-1} are linked to the stretching of hydroxyl groups which are involved in the intramolecular and intermolecular hydrogen bonds in PVA and micro cellulose [6,22,23]. Incorporation of MWCNTs provided reducing of free –OH groups in the hybrid composite structure. Therefore, the straight band appeared with the increase of MWCNTs level. The absorption band between 2840 and 3000 cm^{-1} refers to the stretching C-H from alkyl groups, which is shifted to lower wave number and its intensity decreased with the addition of MWCNTs and micro cellulose [23]. This was mainly attributed to reaching maximum level in bonding formation by free –OH groups of cellulose and carboxyl groups of MWCNTs.

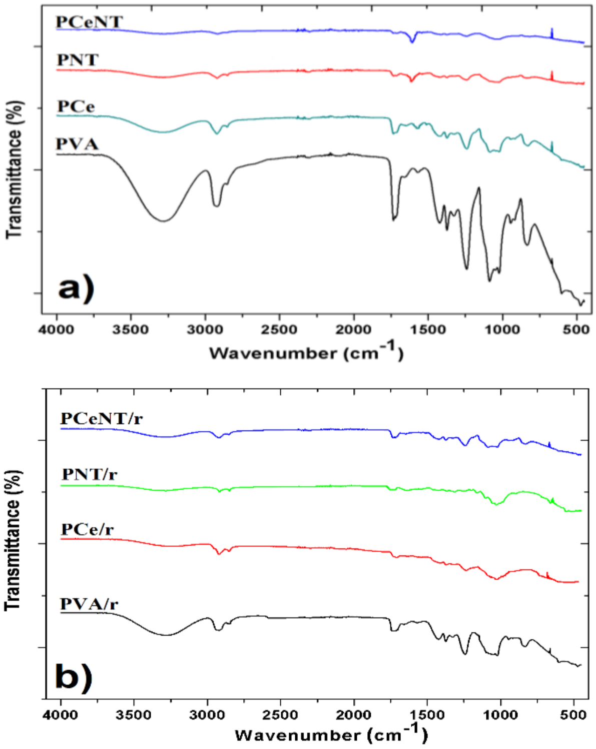
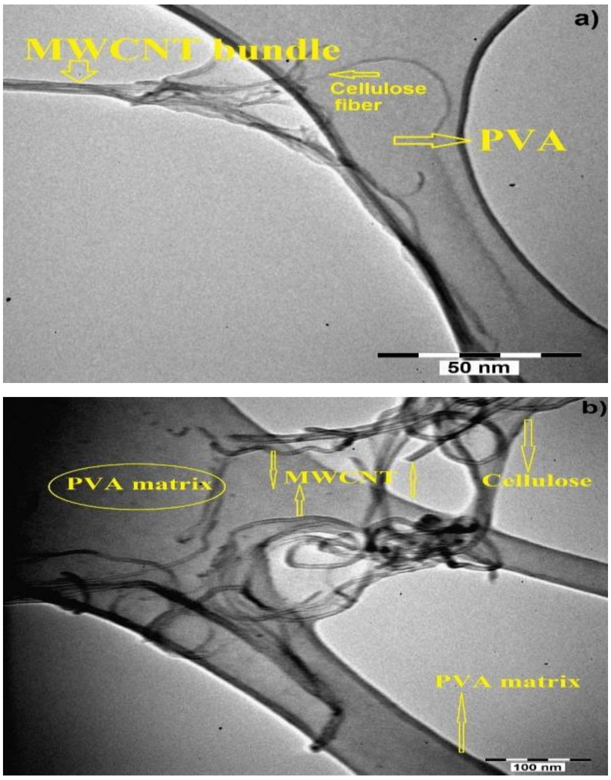


Figure 5. FTIR spectra results of composite films a) primary composite film's FTIR spectra b) reprocessed film's FTIR results

When the reprocessing effect was taken into consideration, the peak verified at 1150 cm^{-1} which were associated neat PVA lost its intensity. This might be attributed to changing the degree of crystallinity of PVA [7,20]. After reprocessing, reinforcements (micro cellulose, MWCNTs and hybrid composition) formed more agglomerated structure (Figure 6) and new molecular interactions change the new crystalline structure of PVA [7]. Influence of MWCNTs has been disappeared near the peak of 1638 cm^{-1}, but micro cellulose maintains its impact near the band of 1055 cm^{-1}. 3200- 3600 cm^{-1} band showed nearly similar band formation with primary reinforced PVA. Consequently, results showed that reprocessing caused intensity decrease on molecular interaction and MWCNTs lost the bonding efficiency in intermolecular level. Therefore, it may cause to lose its superior effect on the hybrid structure at the macro level.

3.4. TEM (Transmission Electron Microscopy) results

TEM analysis was used to evaluate the structure of PVA composite at the nano level. Dispersion of MWCNTs and bonding formation between PVA matrix and reinforcements were observed by using TEM. Figure 6 represents the images of the PVA matrix reinforced with micro cellulose and MWCNTs. It is clear that, while MWCNTs exhibited a straight shape in regions where the dispersion is better (Figure 6a) and it transformed into helix-like shape with increasing agglomeration ratio (Figure 6b). These formations come together and form a cluster (Figure 6c). Mallakpour et al. [5] reported about amino acid functionalized MWCNTs which incorporated into PVA matrix. They stated that the coils structures in MWCNTs formed as a result of hydroxyl group interaction of PVA matrix and amino acid functionalities on the surface of f-MWCNTs. Similar results are available in reprocessed composites for this case. It is clearly seen in Figure 6c and d, interactions between components of composite caused agglomeration. Figure 6 also revealed that reprocessed hybrid composite structure was formed by hybrid cluster core and its micro cellulose and MWCNTs extensions. This formation provides strong bonding and good interaction in the interface of the composite.



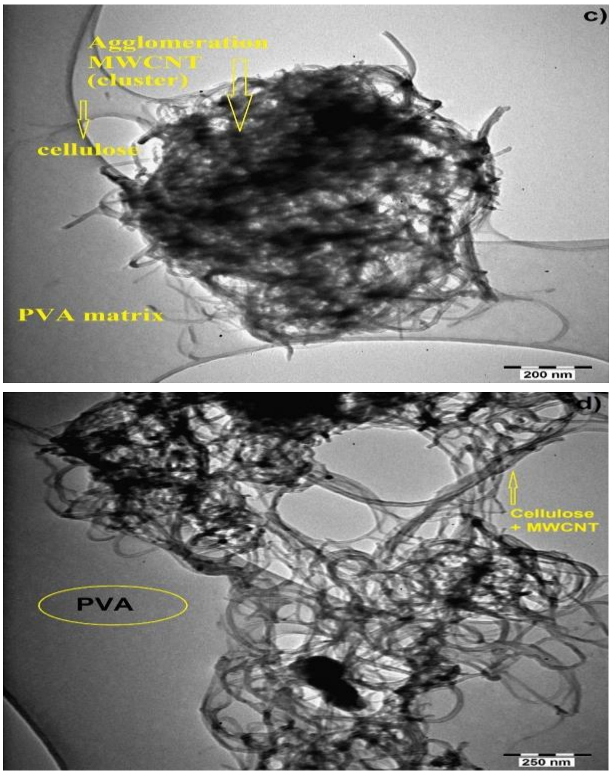
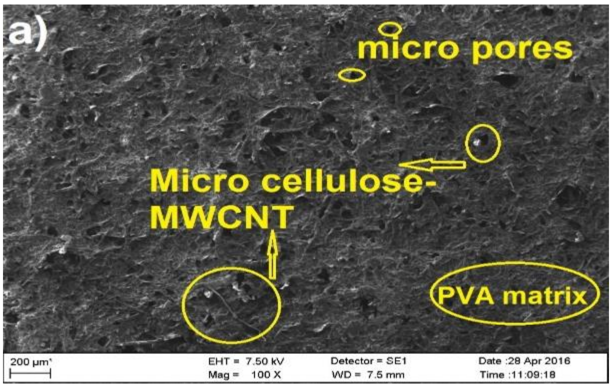


Figure 6. TEM micrograph of composites a) micro structure of PCeNT composite film b) twisted shape of reinforcements (PCeNT) c) agglomeration of reinforcement d) link between reinforcements

3.5. SEM (Scanning Electron Microscopy) Results

Scanning electron microscopy was used to investigate the dispersion of the reinforcements in the composite samples. Figure 7 depicts the hybrid composite film surface (PCeNT) in large and narrow scale. While Figure 7a) shows the rougher surface which contacted with air in the Petri dish during the drying process, Figure 7b) represents the bright surface which contacted with Petri dish surface during the drying process. However, it is observed that both surfaces exhibited different size of pore-like structures with mostly dark color. This was mainly attributed to the accumulation of MWCNTs on pore-like surface.



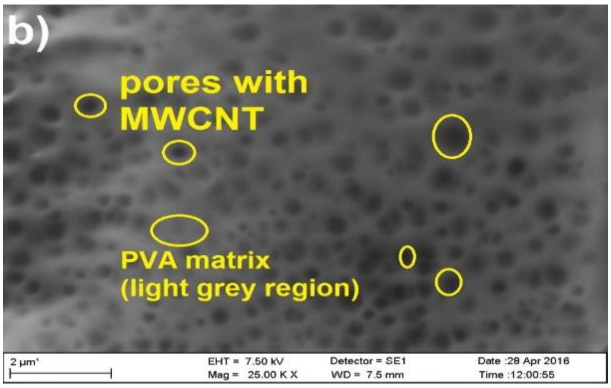


Figure 7. SEM micrograph of PCeNT a) rougher surface of composite film b) pore-like formations of surface

Figure 8 exhibits the cluster formation and linking between micro cellulose-MWCNTs reinforcement. The apparent formation was supported by TEM results that are mentioned before. Amrin et al. [1] reported similarly that when the concentration of CNT (carbon nanotube) is increased the clusters begin to form larger agglomerates. Figure 8a) clearly indicated that micro micro cellulose-MWCNTs have a core-like cluster and each of this form link with their extensions to PVA and each other. It may carry more efficient load transfer to the matrix from reinforcement. Figure 8b) shows also inner structure of the film in narrow scale.

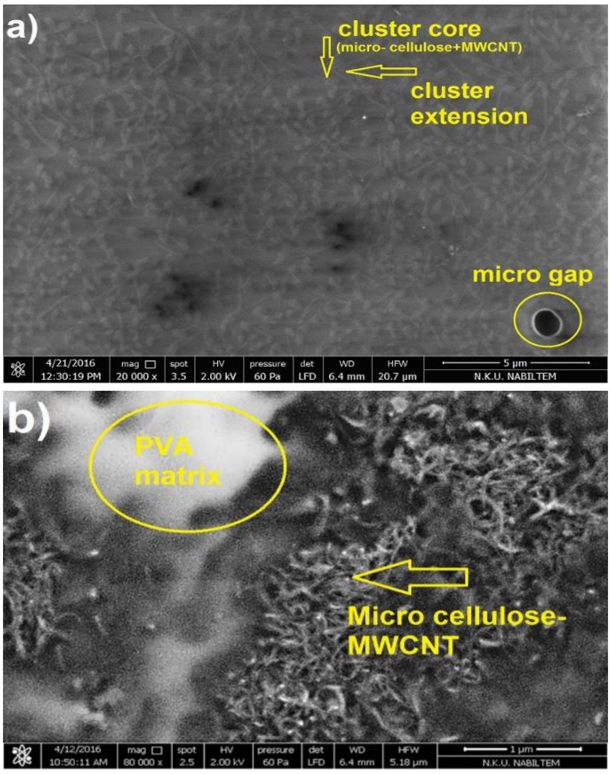


Figure 8. Surface micrograph of composite film (PCeNT) a) linking between reinforcements b) inner structure of composite film

The effect of reprocessing is shown in Figure 9. Figure 9a-b depicts PNT/r and PCeNT/r, respectively. As it can be observed in Figure 9a), PNT/r exhibited lower agglomeration on the surface than PCeNT/r composite. This was mainly attributed to weakened bond structure between reinforcement and PVA matrix. During the reprocessing for the hybrid composite, PVA dissolves easily in water but the bonding between micro cellulose and MWCNTs is still ongoing due to not enough process time. Therefore, micro cellulose-MWCNTs aggregates in PVA matrix.

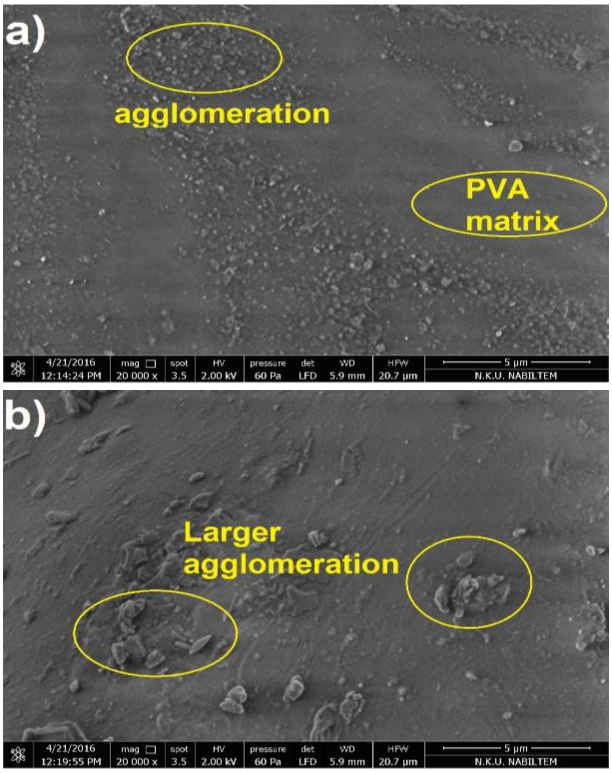


Figure 9. Surface micrograph of reprocessed PVA composite films a) lower size of agglomeration (PCeNT/r) b) larger size of agglomeration (PCeNT/r)

3.6. Optical properties of PVA composite films

Figure 10 shows the UV-Vis absorption spectra of PVA and composite films. Incorporation of reinforcements (MWCNTs, micro cellulose or both) caused strong transparency loss even though the reinforcement content was only 5 wt %. Most of the transparency loss is due to the presence of MWCNTs [9,21]. As it was observed in Figure 10a), the large amount of incident light was absorbed by the components of film and absorbance line started between values of 2.5-3.0. While the neat PVA exhibited a shoulder peak at 298 nm, composite films showed broadband between 200-450 nm. This is attributed to the extended π-conjugated system of the MWCNTs sidewalls [9,21]. All composites exhibited nearly similar band configuration and slope of chart lines. UV-Vis and morphological results are considered together, reinforcement showed good dispersion through the composite film. Absorbance peaks of composite films located at 200-400 nm that is narrower according to primary production films. The starting point of absorbance line declined to about 1.80-1.90. This result indicates that incident light has not been reflected and refracted by the reinforcement through the film. This may be attributed to agglomeration of micro cellulose and MWCNTs which caused in-homogeneous dispersion in composite film.

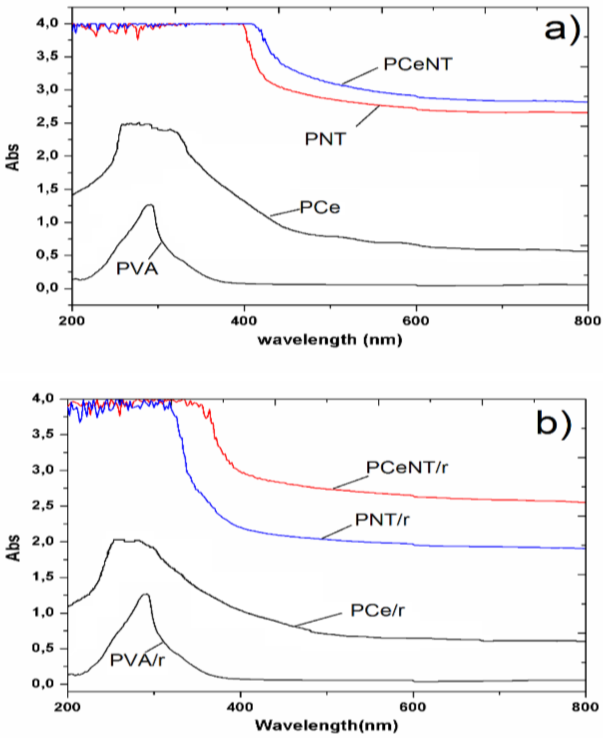


Figure 10. UV-Vis properties of PVA composite films a) absorbance characteristic of primary production films b) absorbance characteristic of reprocessed films

3.7. Mechanical results

Tensile tests were performed to determine the contribution of micro cellulose, MWCNTs and hybrid composition to the strength of PVA composite films. Representative stress–elongation at break curves of composite films with various reinforcement types are shown in Figure 11. Table 3 also represents the tensile test results of composites and reprocessed composites. The neat PVA film showed the maximum stress of 29 MPa and elongation at break of 194 %. The tensile stress of micro cellulose and MWCNTs reinforced PVA composite was improved about 2.5 times and elongation at break decreased about eight times according to the neat PVA film. While Young's modulus of the neat PVA was 984 MPa, hybrid composite showed 1954 MPa modulus value. These results indicated that the hybrid composites exhibited much higher tensile strength and Young's modulus and more rigid features with higher load-bearing capacity.

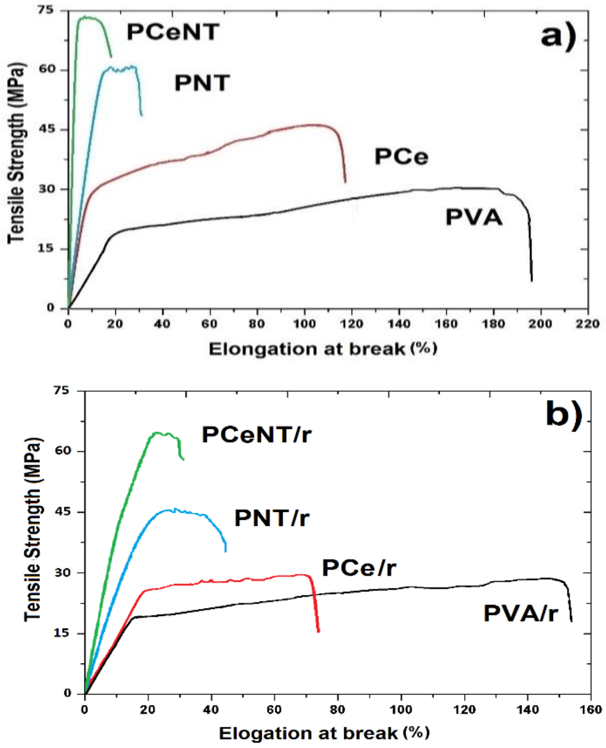


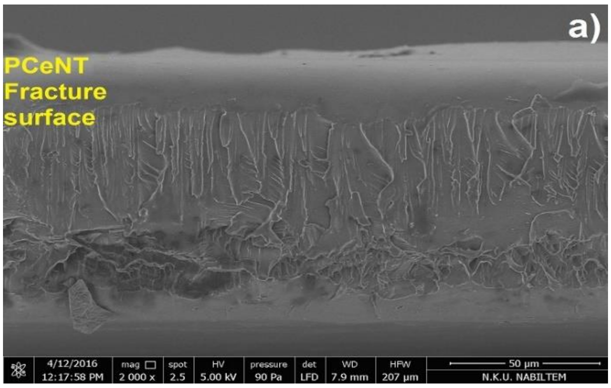
Figure 11. Tensile properties of PVA composite films a) representative stress- elongation at break graph of primary production composites b) changing of tensile graph of reprocessed composites

Table 3. Tensile properties of fabricated PVA composite films

Sample ID	Tensile Strength (MPa)	Elongation at Break (%)	Young's Modulus (MPa)
PVA	29±3.5	194±11.8	984±62
PCe	46±3.7	119±9.4	1435±55
PNT	61±7.7	31±5.7	1688±84
PCeNT	73±6.4	21±1.1	1954±96
PVA/r	26±2.8	156±7.6	891±42
PCe/r	29±3.9	72±6.4	1128±63
PNT/r	45±4.1	44±5.2	1271±77
PCeNT /r	63±4.8	33±2.7	1562±87

As already mentioned before, micro cellulose and MWCNTs formed strong hydrogen bonding with PVA matrix due to the presence of larger hydroxyl groups on their surface. These structures cause good adhesion and efficiently load transportation between matrix and reinforcement. Mallakpour et al. [5] reported results supporting this phenomenon for MWCNTs reinforced PVA composites. It was demonstrated that incorporation of 5% MWCNTs provided an improvement on tensile strength and Young's modulus about 120% and 66%, respectively (the neat PVA; tensile strength 29.7 MPa, elongation at break 164.1%). Another research [24] suggested that higher cellulose nanofiber content in PVA resin exhibited better mechanical properties. The nano-cellulose (40 wt %) impregnation provided 1.5 times higher tensile strength and the decrease of strain from 200% to 30% according to neat PVA resin. The study also revealed that nano-cellulose content is not expected to reinforce composite film due to the presence of possible stress concentration of inner structure [16]. In this case, it was detected that embedded micro cellulose or MWCNTs in matrix improved the mechanical strength due to possible mechanical interlocking, change of matrix crystallinity, or good interfacial adhesion as in similar studies. Micro cellulose bonded both PVA and MWCNTs and formed the reticulated structure which exhibited better mechanical properties (Figure 12a). It can be stated that micro cellulose acted like crossover connection between PVA and MWCNTs in hybrid composite structure.

Considering the effect of reprocessing, reprocessed neat PVA showed a slight change in mechanical properties. Specifically, no differences were observed in tensile strength (26 MPa). In a similar manner, Young's modulus (891 MPa) had also minor change (approximately 8%). This may be attributed to changing of crystallinity after reprocessing [3,8,20]. If the mechanical properties of composite films are to be addressed, lower strength values are encountered compared to the primary production films. The hybrid micro cellulose and MWCNTs reinforced composite showed a tensile strength value about 63 MPa according to reprocessed neat PVA. However, it was 12% lower than primary production hybrid PVA composite. This was mainly attributed to cluster like structures (Figure 9) which cause stress concentrations in the interface of the composite [24,25]. These formations lead to the decrease in mechanical properties. The weak mechanical interlocking and load transfer between matrix and reinforcements were observed due to poor adhesion. As shown in fracture surface of films (Figure 12b), insufficient reinforcement wetting and agglomeration caused weak regions which acted like a notch. Consequently, in spite of the same production conditions, different characteristic behaviors of the components have prevented getting similar mechanical properties.



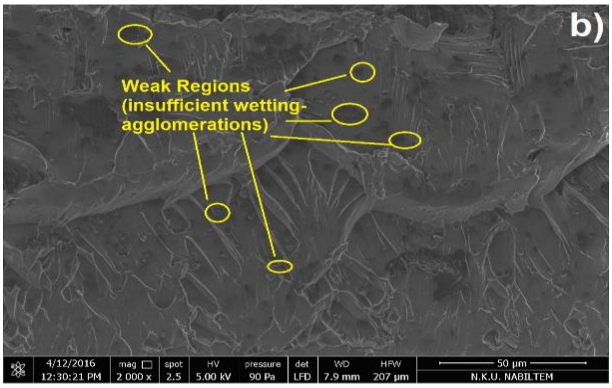


Figure 12. SEM micrograph of composite films a) fracture surface of PCeNT b) weak regions of fracture surface of reprocessed composite film

4. CONCLUSION

In this study, solution casting method was used to produce PVA hybrid composite films. MWCNTs, micro cellulose, and hybrid composition were used as a reinforcement material. Even though the lower content of reinforcement was used, the remarkable enhancement was obtained in hydrophilicity and mechanical properties. Reprocessed composite films exhibited lower strength than primary production composites. However, the strength of reprocessed composites was conspicuously higher than neat PVA. Morphological results revealed that as primary production composite films exhibited more homogeneous dispersion, reprocessing caused agglomeration inner structure.

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