

PREPARATION AND APPLICABILITY OF EVOH/TiO₂ NANOCOMPOSITES PREPARED BY SIMPLE SAPONIFICATION METHOD

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Abstract

The nanocomposite powders of EVOH/rutile-TiO₂ (EVOH/TiO₂-R) and EVOH/anatase-TiO₂ (EVOH/TiO₂-A) were prepared by a solution-precipitation and saponification method. Poly(ethylene-co-vinyl acetate) (EVA)/TiO₂ toluene suspensions were precipitated and saponified in ethanol/KOH solution in a heterogeneous manner. As the saponification time increased, the surface of the nanocomposite particles is eroded and the larger particles are delaminated and fractured into smaller particles due to changing matrix polymer polarity. After 6h saponification time, the particle shape recovered was almost the same as the pristine TiO₂ particles. Preparation, properties and applicability of the prepared nanocomposites were evaluated.

1 Introduction

Polymer nanocomposites are increasingly desirable as coating, packaging, filtering and structural materials in a wide range of aerospace, automobiles, membrane, and electrical engineering applications [1-5]. This is due to our increased ability to analyze, synthesize, and manipulate a broad range of nanofillers and significant investment by laboratories and research centers in industry, government, and academia. Moreover polymers possess general advantages of low cost, lightweight, design flexibility, easy processing, and corrosion resistance. The polymer nanocomposites are one kind of composite materials comprising of nanometer-sized particles, typically at least one dimension less than 100nm, which are uniformly dispersed in and fixed to a polymer matrix. In this way, the nanoparticles are acting like additives to enhance performance and thus are also termed nanofillers or nano-inclusions [6]. Because they have extremely high surface area to volume ratios and alter the mobility of polymer chains near their interfaces, even a small addition of nanoparticles has the potential to drastically transform the properties of the polymer matrix.

Recently, our group has developed a process of simple saponification to make vinyl alcohol (VOH) containing nanocomposites [1, 3]. In this process, at least one vinyl acetate (VAc) containing polymer or blend is dissolved in an appropriate solvent and a suitable viscosity of the solution is achieved. An inorganic nanofiller was dispersed in polymer solution and then the suspension was precipitated and saponified in alkaline non-solvent. This causes separation of the heterogeneous polymer suspension into a solid nanocomposite and liquid solvent phase.

After rinsing off the coagulant and drying, the nanocomposite particles shape was recovered almost the same as the pristine nanofiller particles. Production parameters that affect the properties include polymer and nanofiller concentration, VAc content in polymer, saponification time and precipitation media. These factors can be varied to produce nanocomposites with altering chemical, thermal and mechanical properties. It was the objective of this paper reported here to use new approaches to produce poly(ethylene-co-vinyl alcohol) (EVOH)/TiO₂ nanocomposites to study their properties and applicability.

2 Materials and testing methods

2.1 Materials

EVA containing 28 wt% vinyl acetate (VAc) segment (EVA 1159, Melt flow index = 18g/10min, density = 0.949 g/cm³) was supplied by Hanhwa Chemical Co., Ltd., Korea. Anatase TiO₂-A nanopowder was obtained from Nano Co., Ltd., Kyungnam, Korea with trade name of NT-22 (particle size = 20 nm, specific area 100 m²/g). TiO₂-R nanopowder (YH-P100, particle size = 15 nm, specific area 50 m²/g) were purchased by Shanghai Huzheng Nano Technology Co., Ltd. (Shanghai, China). All fillers were pre-dried in a convection oven for at least 12h at 100°C to remove any moisture from the powders before processing.

2.2 Preparing of EVOH/TiO₂ nanocomposite powder

The EVA pellets (100 g) were first swelled in toluene (900 g) at room temperature for 12 h and followed by heating at 60 °C for 4h. The required amount of TiO₂-R and TiO₂-A was each dispersed in the 10 wt% toluene solution of EVA at room temperature by mechanical premixing and bath sonication for 2 h. 20 ml of diluted suspensions (5.0 wt% in toluene) were saponification by dropwise addition to 200 ml of 0.5 M KOH/ethanol solution. The heterogeneous solution was stirred at room temperature for ambient time, and then the suspension was filtrated, and filtrate washed with methanol. The filtrate was dried under vacuum at 60 °C to a constant weight.

2.3 Tensile test procedure

Dumbbell specimens for tensile tests were prepared in accordance with IEC 60811-1-1 specification. The specimens were preconditioned to 20 % relative humidity and 20 ± 2 °C in order to standardize test conditions. Tensile properties of samples were determined with a universal test machine (UTM, Model DEC-A500TC, Dawha test machine, Korea) at a cross head speed of 250 mm/min. The mean value of at least five specimens of each sample was taken, although specimens that broke in an unusual manner were disregarded.

2.4 Shake flask test

The antibacterial activity of the nanocomposite powders was tested against *Staphylococcus aureus* (*S. aureus*, ATCC 25923) and *Escherichia coli* (*E. coli*, ATCC 25922) with the shake flask method. The bacteria were subcultured on nutrient broth and incubated for 20 h at 37 °C. The cells were suspended in 50 ml of phosphate-buffered saline (PBS) to yield a bacterial suspension of 4.88×10⁷- 4.65×10⁸ colony forming units/ml (cfu/ml). The sample powder (1 g) was weighed and shaken in 20 ml of a bacterial suspension for 24 h. The suspension (50 wt/vol%) was serially diluted in PBS and cultured on nutrient broth at 37 °C for 24h. The number of viable organisms in the suspension was determined by multiplication of the number of colonies with the dilution factor, and the percentage reduction was calculated on the basis of the initial count.

3 Results and Discussions

Figure 1 shows the SEM micrograph of TiO₂-R and TiO₂-A nanopowders. SEM image of the pristine nanopowders showed a primary particle-size ranging from 15 to 35 nm, although agglomerated particles may be several time larger. TiO₂-R contained some impurities which

are corresponding to Al (1.14 wt%) and Si (0.71 wt%). TiO₂-A also showed very low S (0.24 wt%) content.

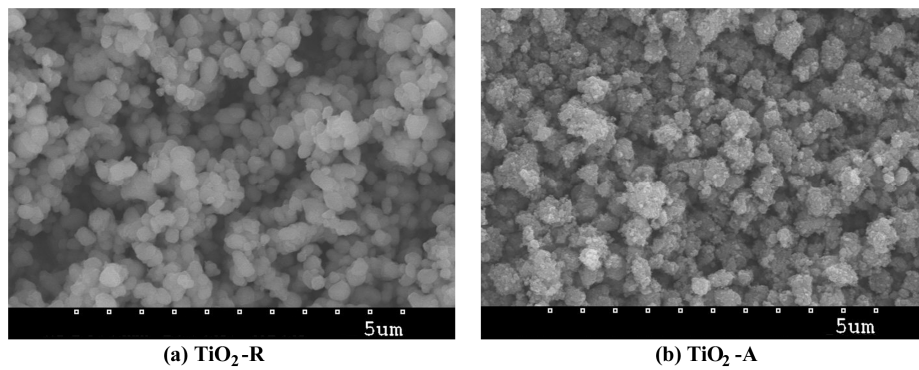


Figure 1. SEM images of the TiO₂-R and TiO₂-A nanopowders.

Figure 2 demonstrates SEM images of the EVA/TiO₂-R50% and EVA/TiO₂-A50% nanocomposites before and after saponification. As shown in Figure 2 (a), TiO₂-R and TiO₂-A particles are randomly dispersed in the EVA matrix. As the saponification time increased, the surface of the nanocomposite particles is eroded and the larger particles are delaminated and fractured into smaller particles due to changing matrix polymer polarity. After 6h saponification time, the particle shape was recovered almost the same as the pristine TiO₂ particles [Figure 2 (b)].

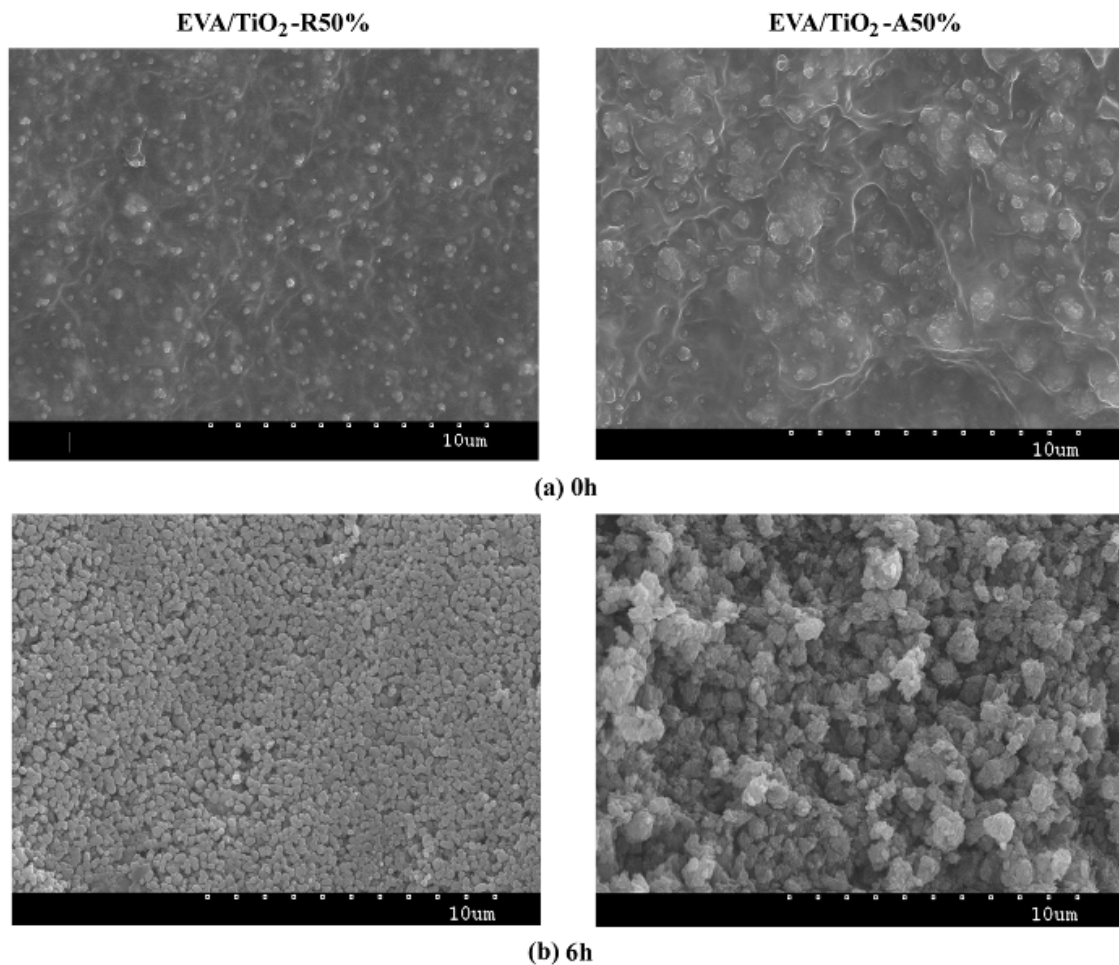


Figure 2. SEM images of the EVA/TiO₂-R50% and EVA/TiO₂-A50% nanocomposite particle surfaces before and after saponification.

Figure 3 and 4 show the DSC melting and crystallization curve of the EVA/TiO₂-R50% and EVA/TiO₂-A50% nanocomposites as a function of saponification time, respectively. As the saponification time increased, the first- and second-scan DSC melting peak of both nanocomposites increased, and the crystallization peak appeared at a higher temperature. It was observed that second-melting point of EVA/TiO₂-R50% and EVA/TiO₂-A50% nanocomposites increases by 17.4 and 15.9 °C, respectively after 6h saponification time. It is noted that first-scan DSC thermogram of EVA/TiO₂-R50%-1h and EVA/TiO₂-A50%-1h nanocomposites showed bimodal melting behavior. The lower melting peak of these nanocomposites should be due to the presence of un-saponified EVA molecules [7]. As the saponification time increased more than 1 h, the lower-melting peak disappeared in the 1st-scan DSC thermogram.

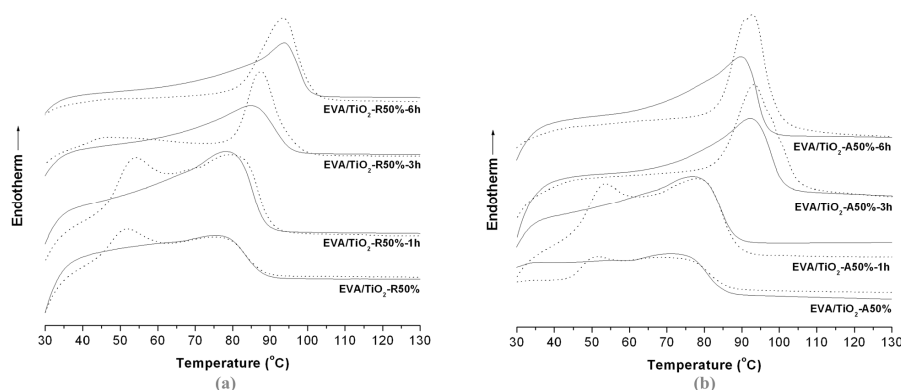


Figure 3. DSC melting curve of the (a) EVA/TiO₂-R50% and (b) EVA/TiO₂-A50% nanocomposites as a function of saponification time (.....: First-scan, ____: Second-scan).

Moreover the highest crystallinity is observed for the two nanocomposites at 1 h saponification time. Even though the T_c of EVA/TiO₂-R50% and EVA/TiO₂-A50% nanocomposites increases by 21.5 and 21.0 °C, respectively after 6 h saponification time, the degree of crystallinity of both nanocomposites lower than that of 1h-saponified ones. This indicated that crystallization of 6h-saponified nanocomposites is strongly inhibited due to the reduction of the polymer chain mobility.

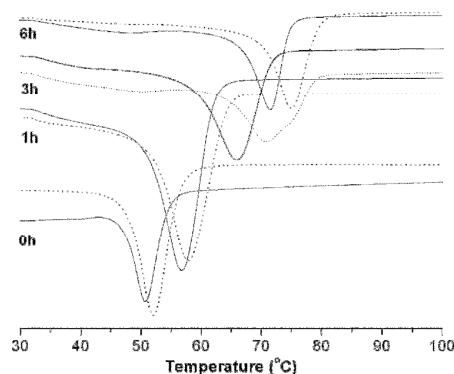


Figure 4. Crystallization behavior of the EVA/TiO₂-R50% and EVA/TiO₂-A50% nanocomposites as a function of saponification time (.....: EVA/TiO₂-R50%, ____: EVA/TiO₂-A50%).

The variation of tensile properties of the EVA/TiO₂-R50% and EVA/TiO₂-A50% nanocomposites as saponification time is shown in Figure 5. The tensile strength of both nanocomposites were significantly increased up to 3 h saponification time and decreased thereafter. At 3 h saponification time, the tensile strength of EVA/TiO₂-R50% nanocomposite was increased by 2.2-fold to 15.4 MPa whereas EVA/TiO₂-A50% increased the tensile strength by 1.9-fold to 13.5MPa as compared to the un-saponified one. This is indicated that saponification process enhances the overall dispersion state of the TiO₂ due to enhanced interactions between the filler and the polymer matrix.

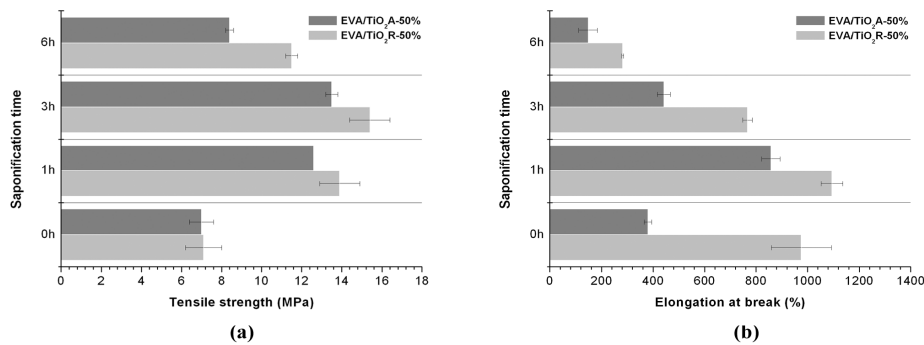


Figure 5. Tensile properties change of the EVA/TiO₂-R50% and EVA/TiO₂-A50% nanocomposites with saponification time.

The elongation at break of the EVA/TiO₂-R50% and EVA/TiO₂-A50% nanocomposites also increased up to 1 h saponification time and thereafter gradually decreased. After saponification for 6h, the elongation at break of both nanocomposites dropped significantly. This significant drop in tensile properties can be explained by reducing flexible rubber regions which provide elasticity and impact resistance.

The antibacterial activity of the nanocomposite powders was tested against *S. aureus* and *E. coli* with the shake flask method in the absence of light. The number of viable bacteria and the percentage reduction of the number of bacteria are summarized in Table 1. It is well known that *S. aureus* and *E. coli* are two of the most common nosocomial pathogens and represent Gram-positive and Gram-negative bacteria.

Sample code	Antibacterial activity			
	<i>S. aureus</i> (+)		<i>E. coli</i> (-)	
	cfu/ml ($\times 10^{-7}$)	Reduction (%)	cfu/ml ($\times 10^{-7}$)	Reduction (%)
Blank	2.80 ± 0.2	-	9.40 ± 0.3	-
TiO ₂ -R	2.19 ± 0.3	21.8 ± 3.0	3.01 ± 0.3	68.0 ± 6.8
TiO ₂ -A	1.51 ± 0.2	46.1 ± 6.1	3.31 ± 0.2	64.8 ± 3.9
Blank	41.1 ± 0.2	-	1.05 ± 0.2	-
EVA/TiO ₂ -R50%	37.0 ± 0.7	10.0 ± 0.2	2.21 ± 0.1	79.0 ± 3.6
EVA/TiO ₂ -A50%	26.1 ± 0.8	36.5 ± 1.1	2.17 ± 0.1	79.3 ± 3.7
Blank	46.5 ± 2.0	-	12.3 ± 1.1	-
EVA/TiO ₂ -R50%-1h	31.0 ± 5.0	33.3 ± 5.4	1.61 ± 0.1	86.9 ± 5.4
EVA/TiO ₂ -A50%-1h	28.2 ± 1.0	39.4 ± 1.4	2.39 ± 0.1	80.6 ± 3.4
Blank	43.5 ± 2.0	-	4.48 ± 0.3	-
EVA/TiO ₂ -R50%-3h	27.2 ± 3.0	37.5 ± 4.1	0.27 ± 0.0	94.5 ± 3.5
EVA/TiO ₂ -A50%-3h	13.7 ± 2.0	68.5 ± 5.0	0.67 ± 0.0	86.4 ± 3.9
Blank	45.6 ± 2.0	-	9.40 ± 0.3	-

EVA/TiO ₂ -R50%-6h	2.43 ± 0.2	94.7 ± 2.0	1.00 ± 0.1	89.4 ± 3.6
EVA/TiO ₂ -A50%-6h	0.50 ± 0.0	98.9 ± 2.0	2.21 ± 0.1	76.5 ± 3.1

Table 1. Shake flask test results for the prepared nanocomposite powder

TiO₂-R and TiO₂-A inhibited the growth of *E. coli* more than *S. aureus*. TiO₂-R extirpated 21.8 and 68.0% of the viable cells of *S. aureus* and *E. coli* whereas for TiO₂-A extirpated 46.1 and 64.8% of the viable cells of *S. aureus* and *E. coli*, respectively. This indicated that *E. coli* is more sensitive to TiO₂ than *S. aureus*.

With the saponification time the antibacterial activity against *S. aureus* of EVA/TiO₂-R50% and EVA/TiO₂-A50% nanocomposite powders was gradually increased. It is noteworthy that 6h-saponified nanocomposites powders exhibits highest antibacterial activity against *S. aureus*. After 24 h of shaking, EVA/TiO₂-R50%-6h and EVA/TiO₂-A50%-6h showed 94.7 and 98.9 % inhibition of the growth of *S. aureus*, respectively. However, these nanocomposites showed significantly different antibacterial activity towards *E. coli* depending on saponification time. EVA/TiO₂-R50% and EVA/TiO₂-A50% nanocomposites were more active on *E. coli* than on *S. aureus* at lower saponification time. It can be also found that the antibacterial activity against *E. coli* of both nanocomposites were increased up to 3 h saponification time and decreased thereafter. This indicated that there was an optimum VAc content for antibacterial activity against *E. coli*. EVA is a random copolymer consisting of ethylene and VAc as repeating units. VAc content has two fundamental effects that influence the properties of EVA copolymers. The first effect is to disrupt the crystalline regions formed by the polyethylene segments of the copolymer. The second overriding effect of VA content results from the polar nature of the acetoxy side chain [8]. In order to inactivate or kill microbes, the nanocomposite particles must come close to or touch the microbes. Such interactions are either attraction or repulsion. As most bacteria carry a net negative surface charge, adhesion of bacteria is discouraged on negatively charged surfaces, while it is promoted on positively charged surfaces [9]. The increase in polarity of nanocomposites after saponification is reflected in the relative polar surface area, hydrogen bond donor, and hydrogen bond acceptor numbers, all of which increase substantially for antibacterial activity.

4 Applicability of EVOH/TiO₂ nanocomposites

4.1 Polymeric fillers

Fillers are commonly incorporated into polymeric resin compositions in order to modify the properties of the resin. However, most inorganic fillers have a naturally hydrophilic surface which is therefore not easily wetted by polymeric resin compositions which are generally hydrophobic. EVOH copolymers have significant potential for polymeric filler and inorganic filler surface modifier due to their combined effect of hydrophilicity, as a consequence of the -OH side groups. Since the materials prepared by this method have excellent antibacterial activity, hydrophilicity, non-toxic, and good mechanical properties, they can be used for industrial applications such like functional fillers for paint and coating materials in aqueous system and antimicrobial filler for polymer compounds

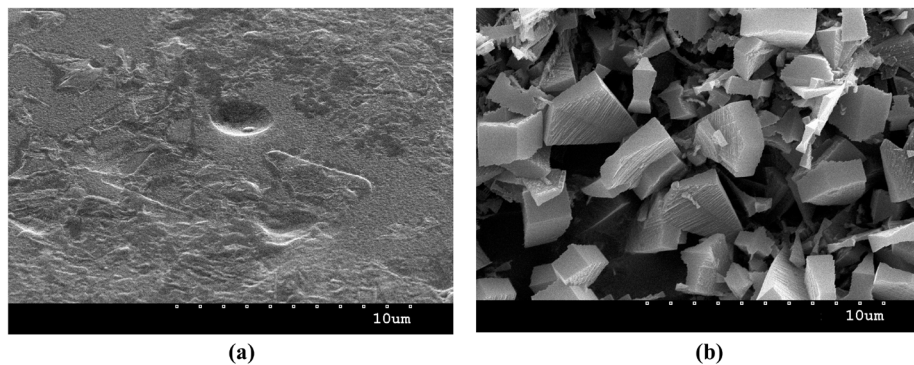


Figure 6. SEM image of the fractured surface of sodium silicate (a) and EVOH/TiO₂/sodium silicate hybrid composites (b) prepared from aqueous coating system.

4.2 Nanocomposites membrane

There is growing interest in photocatalytic degradation of recalcitrant pollutants in wastewater. TiO₂ nanoparticles have also been used in water treatment membrane technology in recent years. Various metal oxides can be used for the photocatalytic reaction, but TiO₂ has attracted considerable attention because of its stability under harsh conditions, commercial availability and ease of preparation [10]. In our previous study, highly porous EVOH particles were prepared by simple saponification method (Figure 7). EVOH membranes have attracted plenty of research interest in fields of biomedical science and water treatment because of its good blood compatibility and hydrophilicity [11]. As noted in the previous section, EVOH/TiO₂ nanocomposites with higher tensile strength were easily prepared by simple saponification method. As such they are of interest for applications such like direct contact membrane distillation, capacitive deionization, and filtration of particles including bacteria and viruses.

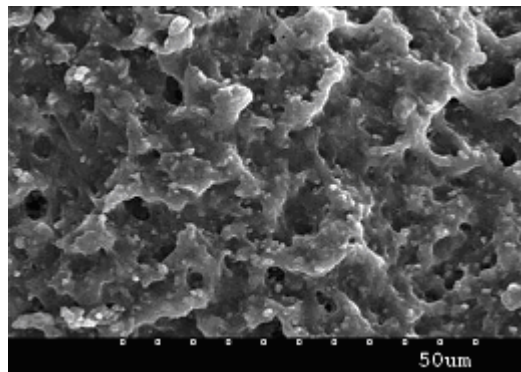


Figure 7. Porous structure of the EVOH/TiO₂ nanocomposite prepared by simple saponification.

4.3 Nanocomposites membrane

In recent years, exceeding many times lead to microbial food safety, food companies are actively taking control measures, and developed a rigorous process and the disinfection system, but the problem of excessive microbial products still occurs. The demand for minimally processed, easily prepared and ready-to-eat fresh food products, globalization of food trade, and distribution from centralized processing pose major challenges for food safety and quality. One possible way to avoid microbial contamination is to develop materials that possess antimicrobial activities. As noted in the previous section, EVOH/TiO₂ nanocomposites with higher antibacterial activity were easily prepared by simple

saponification method. It can be also seen from Figure 8 the nanocomposites also have excellent antifungal activity. The use of simple saponification technology to minimize food losses and provide safe and sound food products has always been the focus of food packaging.

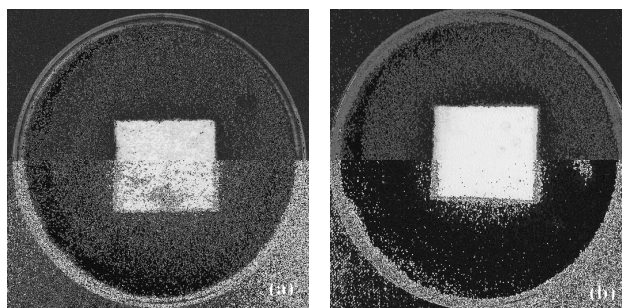


Figure 8. Antifungal activity test results for (a) EVOH/TiO₂-A50% and (b) 3 h saponified EVOH/TiO₂-A50% against *Aspergillus niger*.

4 Acknowledgments

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