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Vinyl ester/C-MMT nanocomposites: investigation of mechanical and antimicrobial properties

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ABSTRACT

Vinyl ester (VE) resins are various applications because of their good resistance excellent and mechanical properties. In this study, red chili particles were incorporated in the sodium montmorillonite (Na^+-MMT) structure and the effect of adding new nanoparticles (C-MMT) on the properties of VE was investigated. The C-MMT was characterized using ultraviolet-visible-near infrared (UV-VIS-NIR) and scanning electron microscopy (SEM). The nanocomposites and VE were investigated by SEM, mechanical and antimicrobial properties. The results obtained from UV-VIS-NIR and SEM confirmed the formation of C-MMT and showed that particles of chili were placed between the layers and also on the surface. The presence of chili in the structure created antimicrobial properties. Chili with capsaicinoids groups can disrupt the activities of bacteria. Therefore, the nanocomposite showed inhibitor and killing against *Bacillus subtilis* and *Escherichia coli*. Also, the results showed that *Bacillus subtilis* was more vulnerable to chili. The results of mechanical properties showed that by increasing the C-MMT content, the mechanical properties are improved.

1. Introduction

In recent decades, the use of polymer coatings has become very popular. Also, the use of nanofillers such as clay, graphene and carbon nanotubes can improve the properties of coatings [1,2]. In the meantime, resins such as VE, epoxy, and epoxy polysulfide are very popular and used in various fields [3-9]. Good elasticity, high thermodynamic flexibility, high resistance to a variety of solvents, self-healing, and good adhesion for many substrates are important properties of these resins [10,11]. Therefore, they can be used in various applications such as adhesives, coatings, composite materials, insulation, and hoses [12-17].

Here, we were able to incorporate chili particles into the Na^+-MMT structure, and then new nanocomposites were prepared using the C-MMT and VE, and the mechanical and antimicrobial properties were investigated.

2. Results and Discussion

Chili, Na^+-MMT, and C-MMT were investigated by UV-VIS-NIR spectroscopy (see Figure 1).

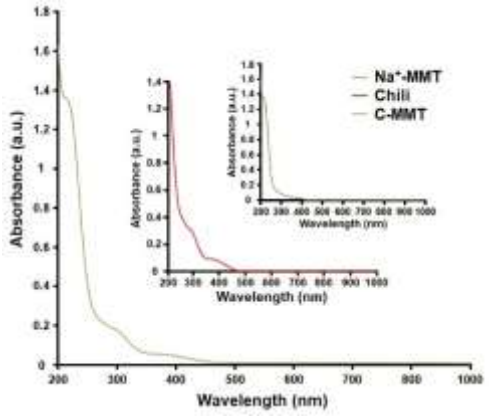

Figure 1. UV-VIS-NIR spectra of Na^+-MMT, chili, and C-MMT.

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In chili spectrum, peaks at 280-300 and 370-450 nm are corresponding to the capsaicinoids groups [18]. Capsaicinoids (Figure 2) are the main compounds found in chili. Also, peak observed at 225 nm for Na^+-MMT assigned to the charge transfer transition of Fe-OH group [19]. Moreover, the C-MMT spectrum shows three peaks, which confirms the formation of the product.

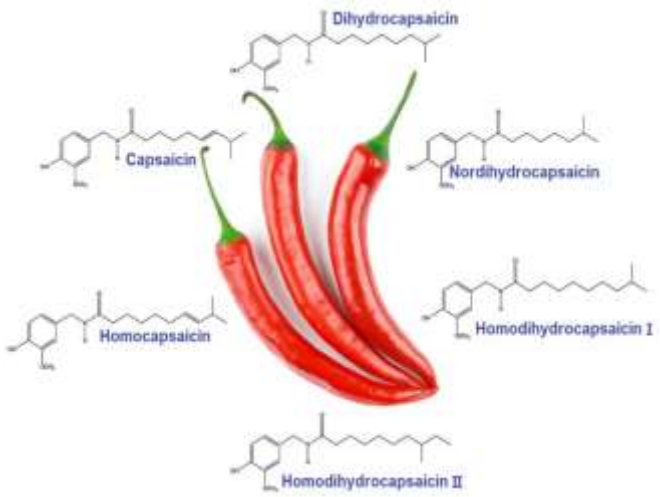

Figure 2. The most important compounds in red chili.

Figure 3 shows SEM images of Na^+-MMT and C-MMT. As can be seen, Na^+-MMT (Figure 3a) has a plate structure and after modification, it also has a plate structure, and chili is located in the interlayer space and to some extent outside the interlayer space. Figure 4 shows SEM images of VE, and VE/C-MMT 3*wt*.%. The surface of VE is smooth (Figure 4a), but the surface of the nanocomposite is partly rough, which is due to the presence of C-MMT in the matrix (see Figure 4b).

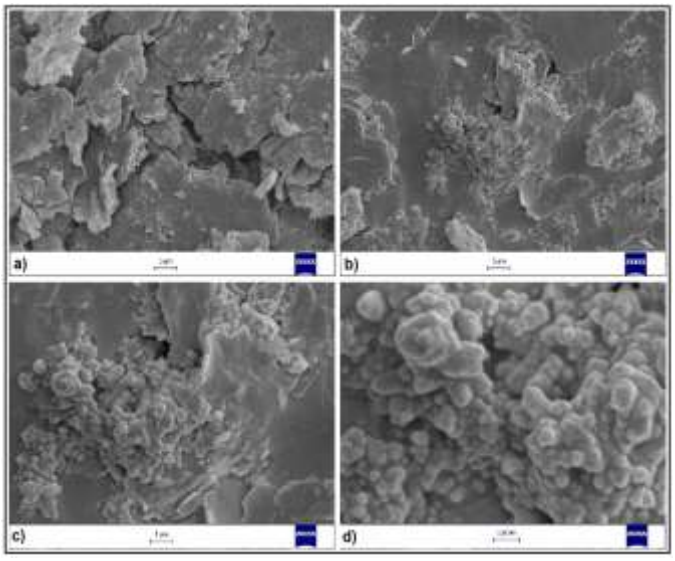

Figure 3. SEM images of samples: Na^+-MMT (a) and C-MMT (b-d).

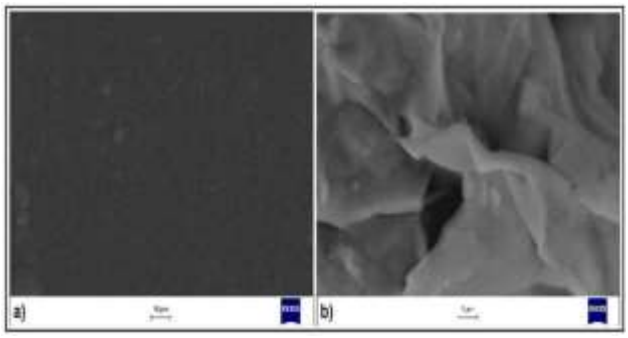

Figure 4. SEM images of samples: VE (a) and VE/C-MMT 3*wt*.% (b).

The mechanical characteristics of the VE, VE/C-MMT 1*wt*.%, VE/C-MMT 2*wt*.%, and VE/C-MMT 3*wt*.% are presented in Table 1. The results show that the mechanical properties are improved by adding C-MMT to the matrix, which is due to the reduction of stress sites in the matrix. In fact, the matrix in the presence of C-MMT can easily eliminate the stress without degradation.

Table 1. Mechanical characteristics of samples

Samples	Strength (MPa)	Elastic modulus (MPa)
VE	49.3 ± 1	1500 ± 10
VE/C-MMT 1*wt*.%	58.6 ± 1	1610 ± 10
VE/C-MMT 2*wt*.%	64.4 ± 1	1740 ± 10
VE/C-MMT 3*wt*.%	69.7 ± 1	1800 ± 10

Over the years there have been extensive efforts to obtain antimicrobial materials among plants, because they can be used in various fields due to their non-toxicity [20,29]. In this study, the antimicrobial properties of VE and VE/C-MMT 3*wt*.% against one types of gram-positive bacteria (*Bacillus subtilis* (ATCC 6633) and one types of gram-negative bacteria (*Escherichia coli* (ATCC 25922) were investigated (see Table 2). As can be see, VE has no effect on microorganisms. But due to the presence of chili in the structure of nanocomposite, inhibition zones are formed. Chili contains compounds that have antibacterial, antioxidant, and anti-inflammatory effects [29,30]. Among these, capsaicinoids groups are related to antibacterial activity [21,29]. Also, due to the simpler cell-wall of gram-positive bacteria compared to gram-negative bacteria [31], chili has a greater effect on *Bacillus subtilis*.

Table 2. Antimicrobial activity of samples

microorganism	DD	MIC	MBC
Bacillus subtilis	-[a]	-[a]	-[a]
	15[b]	500[b]	1000[b]
Escherichia coli	-[a]	-[a]	-[a]
	7[b]	1000[b]	2000[b]

Note:
* DD: Disk diffusion method, inhibition zones in diameter (mm) around the impregnated disk.
** DD: 600 µg per well
*** MIC: minimum inhibitory concentration
MBC: minimum bactericidal concentration
**** Concentrations of MIC and MBC as µg/mL
***** [a]VE, [b]VE/C-MMT 3*wt*.%

3. Experimental

3.1. General

The inorganic clay was Na^+-MMT were obtained from Rockwood Company (USA). VE resin (v301) were obtained from Farapol jam company (Iran). Also, the curing agent was methyl ethyl ketone peroxide and the catalyst used was cobalt naphthenate/N,N-dimethylaniline, which were obtained from Sigma-Aldrich. Moreover, styrene was supplied from Merck. Red chili powder was purchased from local markets (Rasht city, Iran) and all other solvents and chemicals were purchased from Merck Chemical s Co. and used as received. UV-VIS-NIR absorption spectra (190-1100 nm, resolution: 0.5 nm) were recorded on a Hanon double beam spectrophotometer. SEM was performed on a sigma VP500 instrument (Germany'S ZEISS Company). Tensile tests were on a SMT-5 tester (Santam, Iran) at a speed of 500 mm/min according to ASTM D638. At least five repeats were performed per each sample, and the mean values were reported. Antimicrobial properties were evaluated using the agar diffusion method according to the procedure described in the literature, and the MIC and MBC were determined [31].

3.2. Modification of Na^+-MMT by chili

The Na^+-MMT was swollen according to the method described in the literature [19]. Na^+-MMT (10 g) was stirred in distilled water (1000 mL) at 25 °C for 24 h. Then, Red chili powder (5 g) was stirred in distilled water (300 ml) at 25 °C for 1 hour and added to mixture of Na^+-MMT. Next, the mixture was stirred at 30 °C for 24 h, then the mixture was rested for 24 h. At last, the mixture was centrifuged (for 10 min at 6000 rpm) and C-MMT was obtained and was vacuum-dried at 25 °C for 24 h.

3.3. Preparation of samples

To prepare the nanocomposites, C-MMT and styrene (to dilute of VE) were added to the VE. Then, the mixture was stirred for 30 min (by mechanical stirrer at 3000 rpm). The mixture was that placed in an oven to remove excess styrene from the resin. Next, curing agent and catalyst were added to the mixture and mixed for 3 min. The mixture was left at 25 °C for 24 h to be cured. Then, the mixture was post-cured at 70 °C for 3 h. The C-MMT content in the nanocomposites was 1, 2, and 3 *wt*.%. A sample without C-MMT was also prepared.

4. Conclusion

To sum up, we prepared nanocomposites based on VE and C-MMT. The results showed that after modification of Na^+-MMT, particles of chili were placed between the layers and also on the surface. Also, with the increase of C-MMT in the matrix, the mechanical properties improved. The results of antimicrobial study showed that C-MMT can be effective against *Bacillus subtilis* and *Escherichia coli*.

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