

Thermal, mechanical, and corrosion resistance properties of vinyl ester/clay nanocomposites for the matrix of carbon fiber-reinforced composites exposed to electron beam

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ABSTRACT: Vinyl ester/clay nanocomposites with 1, 3, and 5% nanoclay contents were prepared. X-ray diffractography patterns and Scanning Electron micrographs showed that nanocomposites with the exfoliated structure were formed. Thermogravimetric analysis, water absorption test, and Tafel polarization method, respectively, revealed the improvements in thermal resistance, water barrier properties, and corrosion resistance properties of the samples with an increase in the amount of the incorporated nanoclay. Tensile tests showed that nanoclay also enhanced the mechanical properties of the polymer, so that the tensile strength of the samples with 5% nanoclay was more than 3 times higher than tensile strength of pure vinyl ester samples. Overall, the best properties were observed for the samples containing 5% nanoclay. Pure vinyl ester and nanocomposite with 5% nanoclay content were exposed to the electron beam radiation and their mechanical properties improved up to 500 kGy irradiation dose. Finally, pure vinyl ester and vinyl ester/nanoclay (5%) matrixes were reinforced with carbon fiber and the effect of electron beam irradiation on their mechanical properties was examined. The tensile strength and the modulus of the samples initially increased after exposure to the radiation doses up to 500 kGy and then a decrease was observed as the irradiation dose rose to 1000 kGy. Moreover, nanoclay moderated the effect of the irradiation. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42393.

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INTRODUCTION

The ever-increasing usage of polymeric materials requires some enhanced properties, which the pure polymers lack. Thus, polymeric composites and nanocomposites have gained much interest as the materials with many tailored properties. Vinyl ester resin is one of the most desirable materials used widely in many composite and nanocomposite manufacturing processes. These low-cost composites possess important material properties in comparison with most unsaturated polyesters.¹

The effects of various particles such as glass flake,² CuO,³ TiO₂,⁴ and carbon nanotubes^{5,6} on vinyl ester resin are reported in the literature. However, montmorillonite (MMT) is the most common filler in this case. MMT is a type of clay with a laminated structure, in which the layers have the thickness of 1 nm. For the synthesis of a potent polymer/MMT nanocomposite, clay particles are usually modified via growth of the basal (inter-layer) spacing by exchanging the metal cations with an intercalating reagent such as alkyl ammonium ions. This will facilitate intercalation of polymer chains into the galleries between the

clay layers, decrease interactions between the MMT platelets, and improve the interaction between the polymer and the clay.

Pashaei *et al.* characterized vinyl ester/MMT nanocomposites for thermal and mechanical properties. They reported that introduction of the nanoclay into vinyl ester matrix increases the thermal stability. Moreover, a decrease in tensile strength and improvement in tensile modulus and surface hardness were noticed with an increase in nanofiller content.⁷ Others^{8–11} also report the improvement of various mechanical and thermal properties due to the incorporation of MMT nanoparticles in vinyl ester resin. Moreover, MMT is effective in reducing the diffusion coefficient and permeability of water through the vinyl ester resin.¹²

Despite the fact that nanoclay can improve the mechanical properties of the polymer, it still cannot fulfill the required properties for some usages. More improvement in mechanical properties could be achieved via reinforcement with carbon fiber. The usage of carbon fiber-reinforced vinyl ester composites is already reported for applications such as naval purposes.^{13,14}

For some applications, it is important to examine the effect of ionizing radiations on the properties of the composite. As an instance, the study of irradiation-induced changes in mechanical properties is a necessity for choosing a polymeric composite to be used in manufacturing of nuclear waste disposal containers. The result of irradiation on the polymer properties depends on the effect of the applied radiation on the structure of polymer chains. In some cases irradiation causes chain-scissioning reactions in polymer structure, while in some other cases it causes cross-linking reactions.

The first objective of this research is to examine the effect of the nanoclay on different properties of the vinyl ester polymers. Thermal, mechanical, and corrosion resistance of the prepared nanocomposites are presented and are compared. Then, the nanocomposite with the best properties was selected for reinforcement with carbon fiber. Finally, the effect of electron beam irradiation on the carbon fiber-reinforced samples was studied.

EXPERIMENTAL

Materials

The resin used to prepare nanocomposites was bisphenol-A-based vinyl ester (Yashm Paint & Resin Co., Tehran, Iran) containing 40% of dissolved styrene. The viscosity of the resin is 350–500 cP at 25°C and its specific gravity is 1.1. Methyl ethyl ketone peroxide (MEKP) as a catalyst, *N,N*-dimethylaniline (DMA) as a promoter, and cobalt naphthenate as an accelerator were also obtained from Yashm Paint & Resin Co. The used nanoclay was commercial treated clay Cloisite 30B supplied by Southern Clay Products Inc. (USA). The MMT clay Cloisite 30B was modified with alkyl quaternary ammonium ions to increase the interlayer spacing, decrease interactions between the MMT platelets, and improve the interaction between the polymer and the nanoclay. The used carbon fiber was vinyl ester sized T300 carbon fiber woven into a plain weave cloth with the surface density of 200 g m⁻² and thickness of 0.25 mm.

Sample Preparation

Vinyl ester/nanoclay composites containing 0, 1, 3, and 5% of nanoclay (named VE, VE1, VE3, and VE5, respectively) were fabricated by using in-situ polymerization method. In the first step, MMT nanoclay was dried at 80°C for 24 h. Then, a relevant amount of it was added to the epoxy resin by 2000 rpm mechanical mixing for 2 h, followed by ultrasonication for 30 min at the room temperature and at the frequency of 40 kHz, using a Wisc WUC-A03H (Germany) ultrasonic bath. Upon completion of degassing, MEKP was added to the mixture while stirring slowly. Cobalt naphthenate and DMA were then added in the same way. The ratios of resin, MEKP, cobalt naphthenate, and DMA in the mixture were 100 : 1.5 : 0.12 : 0.15 by weight, respectively. The obtained mixture was cast in the silicon molds, which were designed in suitable shapes and sizes in accordance with each testing method. Finally, molded nanocomposites were cured at room temperature for 24 h and were postcured at 100°C for 2 h.

The carbon fiber-reinforced nanocomposites were manufactured by hand lay-up method. In this method, a Teflon film was placed on the surface of a steel mold plate to avoid the polymer

being stuck to the surface. Carbon fibers in the form of woven mats were cut as per the mold size and the first carbon fiber layer was placed on the surface of the mold after inserting the Teflon film. Then the mixture of vinyl ester resin, nanoclay, and curing agents that had been prepared via the previously mentioned method was uniformly spread on the mat surface with the help of a brush. The second layer of mat was then placed on the resin surface and a roller was moved with a mild pressure on the mat–resin layer to remove any air trapped as well as the excess resin present. The process was repeated for each layer of resin and mat, until eight layers were stacked. After placing a Teflon film, the top mold plate was placed on the stacked layers and the pressure was applied to the stack by a press. Curing process was gone through under the applied pressure at the room temperature. After curing for 24 h, the mold was opened and the developed composite was taken out and postcured at 100°C for 2 h. Finally, completely cured composite part was cut to produce the required specimens. Two types of carbon fiber-reinforced composites samples were prepared in this step. The first type (named VF) was produced using pure vinyl ester resin and the second type (named VFC) was produced using the mixture of vinyl ester resin and 5% nanoclay.

Irradiation

Samples were irradiated in the Yazd Radiation Processing Center (Iran) by means of a Rhodotron-TT200 electron accelerator (IBA Co., Belgium), in air atmosphere and at the doses of 100, 500, and 1000 kGy. Rhodotron-TT200 produces a 10 MeV electron beam with maximum current of 10 mA using 107 MHz RF in a coaxial cavity with an outer diameter of 208 cm. Nine deflecting magnets reinject the electrons into the cavity after each pass. In each pass, electrons obtain 1 MeV energy. Consequently, after 10 passes through the cavity diameter, their energy reaches 10 MeV. Then, produced electrons are sent to a vertical scanning horn with a scan width of 100 cm. Samples pass under the scanned beam by a variable-speed conveyor. Different irradiation doses could be obtained via changes in the conveyor speed and the number of passes.

XRD

Vinyl ester/clay nanocomposites structure (intercalated or exfoliated) was investigated by a Phillips X'Pert X-ray diffractometer which uses CuK_α radiation ($\lambda = 1.542 \text{ \AA}$) and operates at 40 kV and 40 mA. The results were generated within the range of scattering angles (2θ) of 0–10° at the rate of 2° min⁻¹ at the room temperature.

Scanning Electron Microscope

The morphology of the vinyl ester/clay nanocomposite specimens was observed on the micrographs obtained by a Philips XL30 scanning electron microscope (SEM). The fracture surface of the samples was coated with a thin layer of gold before scanning.

Thermogravimetric Analysis

Thermal stability of the nanocomposite samples has been investigated using Rheometric Scientific STA 1500 Instrument (USA). About 10 mg of a sample was heated at the rate of 10°C min⁻¹ with Argon as a purge gas (flow rate, 30–35 mL min⁻¹) to obtain the dynamic thermogravimetric analysis (TGA) scans.

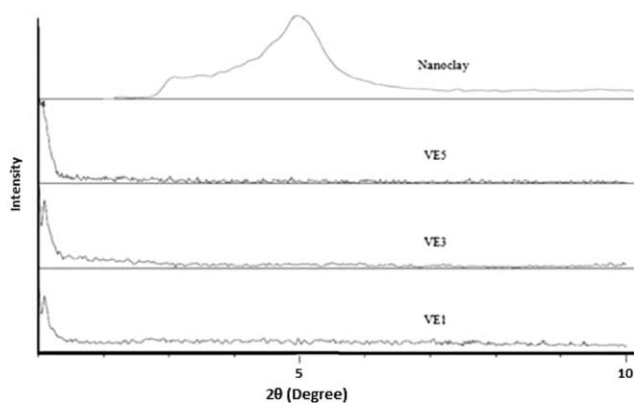


Figure 1. XRD patterns of nanocomposites.

Water Absorption

Water absorption studies were carried out on disc specimens, 50 mm in diameter and 3 mm in thickness, for 24 h using the ASTM D570 method for water absorption of plastics. The specimens were initially weighed, then placed in a container of demineralized water at the room temperature. The specimens were removed from the storage water after 24 h, blotted dry, and reweighed. The amount of the absorbed water was calculated via difference in primary and final sample weights.

Chemical Resistance

The effect of corrosive chemical media on nanocomposite samples was examined via electrochemical measurements. In this case, Tafel polarization measurement was performed in a traditional three-electrode cell system using Autolab PGSTAT302N with GPES Software (Netherlands). In the three-electrode cell assembly, nanocomposite specimen was taken as a working electrode, Pt as a counter electrode, and Ag/AgCl as a reference electrode. The tests were conducted in 40% HNO₃ solution at the room temperature. Tafel plots were obtained by potentiodynamic polarization at a scan rate of 1 mV s⁻¹. The plots were then used to obtain the values of corrosion potential (E_{corr}), corrosion current density (I_{corr}), and polarization resistance (R_p).

Tensile Testing

Tensile testing was carried out to determine the mechanical properties of vinyl ester/nanoclay composites before and after reinforcement with the carbon fiber. The effects of electron beam irradiation on the reinforced specimens were also studied. ASTM D638M and ASTM D3039M methods were used to prepare the vinyl ester/nanoclay tensile testing specimens and carbon fiber-reinforced tensile testing specimens, respectively. Tensile tests were performed using an SANTAM STM50 (Iran) testing machine to determine the elastic modulus and tensile strength of each sample. The cross-head speed was set at 1 mm min⁻¹. Five specimens were utilized for each specific material and the average of their results was reported.

RESULTS AND DISCUSSION

Morphology

The XRD scans of nanoclay and nanocomposite samples containing 1, 3, and 5% of nanoclay are illustrated in Figure 1. The

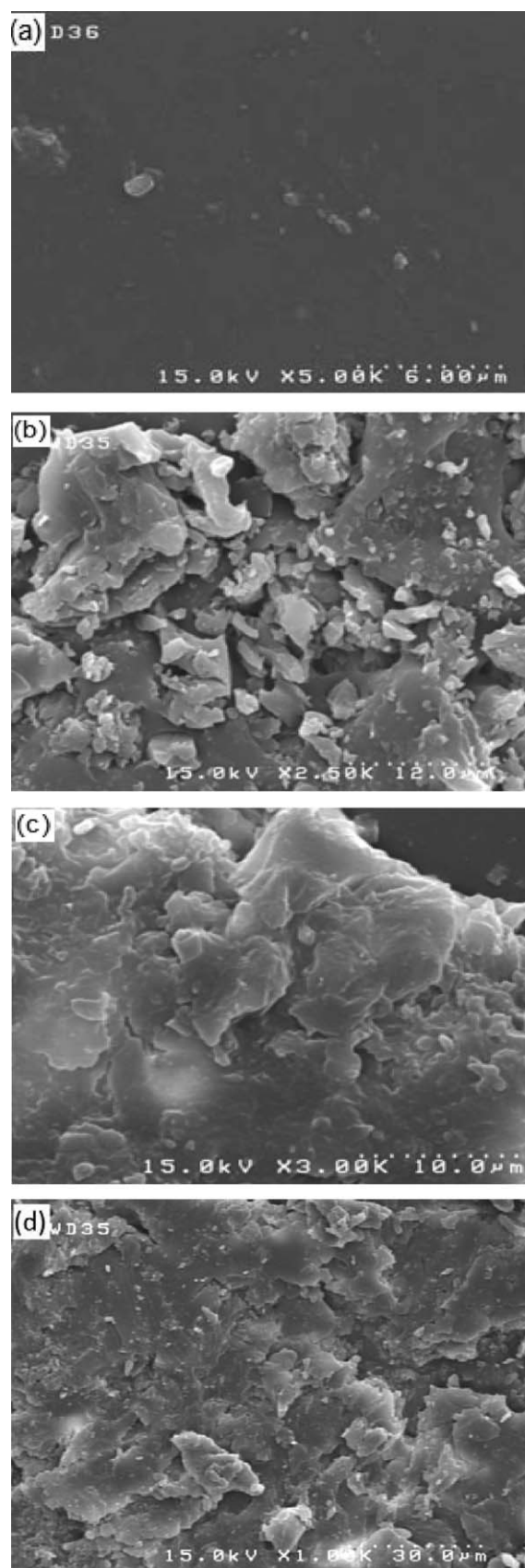


Figure 2. SEM image of (a) Neat vinyl ester polymer, (b) VE1 nanocomposite, (c) VE3 nanocomposite, (d) VE5 nanocomposite.

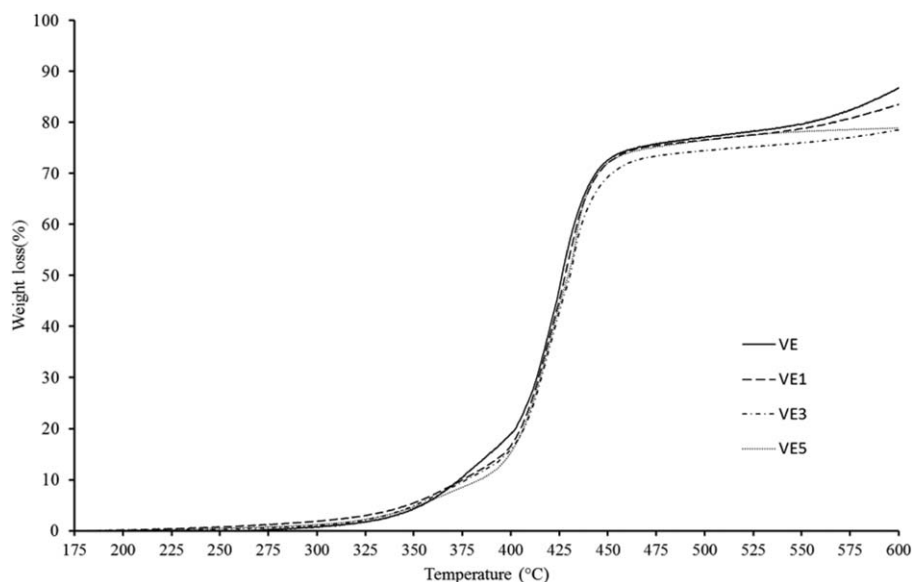


Figure 3. TGA thermograms of vinyl ester/clay nanocomposites.

XRD pattern of the nanoclay has a peak at a 2θ value of 5.11° corresponding to an intergallery spacing of 17.3 \AA . The disappearance of peaks implicates the exfoliation and random dispersion of the nanoclay layers in polymeric matrix. During the mechanical mixing and ultrasonication, the polymeric resin exfoliated between the intergallery spacing of nanoclay and made the nanoclay layers move apart. Exfoliated structure that is detected in the prepared nanocomposites shows that the nanoclay platelets completely dispersed in the vinyl ester matrix because of the proper mixing.

Figure 2 presents the SEM micrographs of the fracture surfaces for the neat vinyl ester resin, and the nanocomposite containing 1 and 3% nanoclay. The picture for the neat vinyl ester resin [Figure 2(a)] illustrates that the neat resin shows a smooth fracture surface failure. This proves a brittle fracture behavior because of the low toughness of the pure vinyl ester resin. Contrarily, Figure 2(b–d) shows the rougher fracture surfaces of the nanocomposites, which account for the improvement on fracture toughness. The observed surface roughness may be due to the exfoliation of nanoclay layers in the vinyl ester matrix. Numerous microcracks at the interface of exfoliated clay layers and vinyl ester matrix are observable on the fracture surface. These microcracks propagate along the nanoclay platelets and provide a highly tortuous fracture surface.

Table I. TGA Data in Argon Atmosphere for Vinyl Ester/Clay Nanocomposites

Sample	$T_{\text{weight loss}} (\%) (\text{°C})$			Ash content (%) at 600°C
	T_{10}	T_{50}	T_{max}	
VE	373	426	422	13.28
VE1	375	429	425	16.48
VE3	376	430	430	21.37
VE5	384	430	433	21.01

Thermal Properties

Thermal stability of nanocomposites was examined by TGA within the temperature range of 25–600°C. Figure 3 shows the TG curves of pure vinyl ester resin and its nanocomposites with 1, 3, and 5% nanoclay. Generally, introduction of nanoclay to a polymeric matrix can improve the thermal stabilities since the nanoclay can hinder the permeability of volatile degradation products by the material. The dispersed clay creates a barrier that delays the release of thermal degradation products in contrast to the pristine polymer. As shown in Figure 3, the weight loss of various nanocomposite samples follows the same trend. According to Xie *et al.*,¹⁵ the TGA curves of the organically modified layered silicates for the temperatures up to 600°C are considered in three parts: (1) the free water region ($T < 200^\circ\text{C}$); (2) the region in which organic substances evolve ($200^\circ\text{C} < T < 500^\circ\text{C}$); (3) the structural water region ($500^\circ\text{C} < T < 600^\circ\text{C}$). Since nanoclay particles had been dried and had been stored in a desiccator before usage, the slight weight loss at temperatures lower than 200°C could be linked to the decomposition of monomers and impurities involved in the polymeric structures. At the higher temperatures, polymer chain

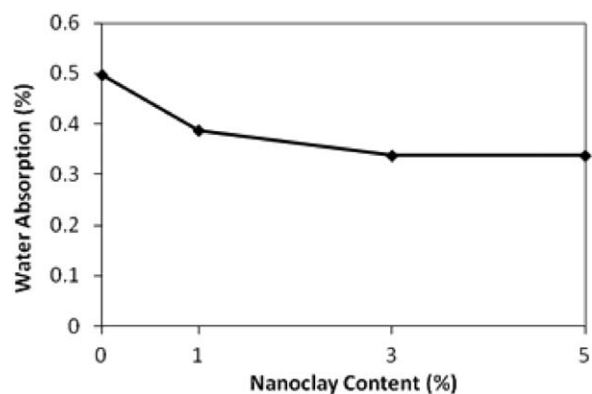


Figure 4. Water absorption of pure vinyl ester polymer and nanocomposite samples.

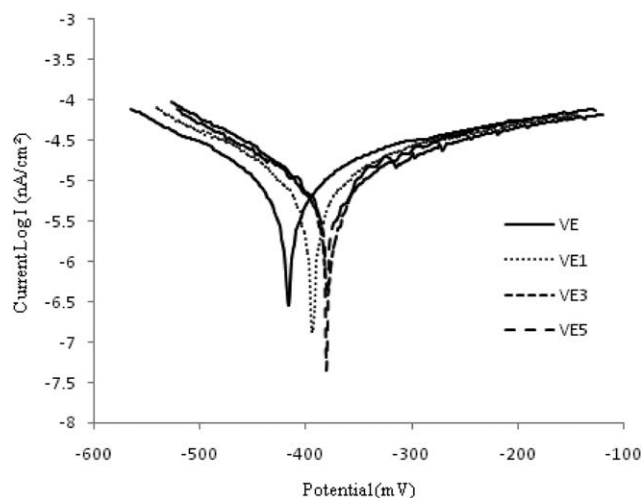


Figure 5. Tafel plots of vinyl ester/clay nanocomposites.

breakages reactions increase along with the decomposition of organic modifiers involved in the nanoclay particles. These reactions result in the increasingly weight loss of the nanocomposite samples. Finally, the weight of the samples decreases slightly due to the few residual polymer decomposition reactions and structural water loss from nanoclay particles.

The relative thermal stability of vinyl ester nanocomposites has been studied via comparison of the decomposition temperatures as different weight loss percentages (Table I). It can be observed from Table I that decomposition temperatures at 10 and 50% weight loss increase with an increase in nanoclay content. This can be attributed to the favorable interaction of polymer matrix and nanoclay particles, resulting in the improvement in thermal stability of polymeric matrix. This improvement could also be noticed in the light of the increase in ash content at 600°C for nanocomposites, when compared with the pure vinyl ester samples.

Water Absorption

In many usages, composite materials are in direct contact with an aqueous environment. Hereby, water absorption may affect various properties of the material or cause damage. Figure 4 shows that the addition of nanoclay can significantly decrease the water absorption of resin matrix. The amount of water absorbed into the pure vinyl ester resin decreased from 0.5 to 0.38% for the nanocomposite containing 1% nanoclay. Water absorption of the samples containing 3 and 5% nanoclay was about 0.34% which shows even more improvement. It seems

Table II. Corrosion Protection Properties of Vinyl Ester/Clay Nanocomposites

Sample	E_{corr} (mV)	R_p (k Ω)	I_{corr} (nA/cm ²)
VE	-416	118	0.25
VE1	-393	126	0.22
VE3	-381	166	0.16
VE5	-380	201	0.15

Table III. Mechanical Properties of Different Vinyl Ester/Clay Nanocomposites

Sample	Tensile Strength (MPa)	Modulus (GPa)
VE	13	0.9
VE1	25	1.7
VE3	34	2.3
VE5	41	2.0

that exfoliated silicate layers work as the barriers to the water diffusion to the material structure.

Corrosion Resistance

The corrosion resistance properties of the vinyl ester/clay nanocomposite samples were evaluated by the Tafel polarization method according to the values of corrosion potential (E_{corr}), polarization resistance (R_p), and corrosion current (I_{corr}) measured after exposure to the 40% HNO₃ solution for 1 h. Figure 5 shows the Tafel plots of the vinyl ester and the vinyl ester/nanoclay samples.

As listed in Table II, the vinyl ester/nanoclay samples exhibited higher E_{corr} values than the pure vinyl ester samples, and they increased with an increase in nanoclay content. The sample containing 5% nanoclay showed an R_p value of 201 k Ω , which was higher than that of the pure vinyl ester (118 k Ω). In addition, the I_{corr} values decreased gradually with an increase in nanoclay loading, revealing that the anticorrosive property of the vinyl ester was enhanced due to the dispersion of nanoclay in the vinyl ester matrix. The enhancement of the corrosive protection effect is attributed to the increase in the tortuosity of the diffusion pathways of O₂ molecules due to the presence of the dispersed silicate nanolayers. Moreover, the nanocomposite containing 5% nanoclay had the highest E_{corr} and R_p , as well as the lowest I_{corr} within the system. This is consistent with the water absorption results, which suggested that the content of the nanoclay silicate galleries in VE5 was the highest and most exfoliated, providing the longest tortuosity of the diffusion pathway among the investigated samples.

Mechanical Properties

Tensile testing method was employed in order to examine the effect of various nanoclay loadings on mechanical properties of vinyl ester matrix. Elastic modulus and tensile strength of each sample are shown in Table III. The incorporation of nanoclay into the resin improved its tensile strength greatly. In the studied range of nanoclay content, the tensile strength of the samples increased with the amount of the incorporated nanoclay. At 5% of nanoclay, the nanocomposite samples had a tensile strength of more than 3 times higher than that of the pure vinyl ester samples. The observed significant improvement of tensile strength was because of the nanoscale dispersion of silicate layers in the polymer matrix and the high interaction between the alkyl ammonium ions and the polymer chains.

The addition of nanoclay to the vinyl ester matrix also increased the elastic modulus. Incorporation of 1 and 3% nanoclay into the polymer provided a modulus 1.9 times and 2.6 times higher than that of the neat resin, respectively. The improvement in

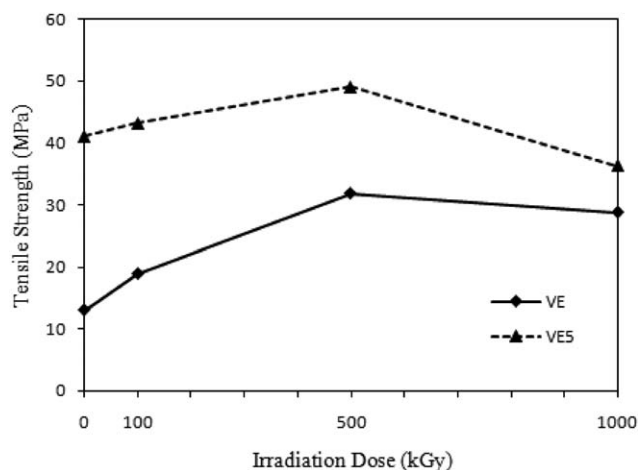


Figure 6. Effect of electron beam irradiation on tensile strength of VE and VE5 samples.

elastic modulus could be due to the exfoliated structure of the prepared nanocomposites and the high degree of dispersion of nanoclay particles that limited the mobility of polymer chains under tension as well as to the good adhesion between the particles and the polymer chains. The optimum rigidity was observed for the samples with 3% nanoclay. In higher nanoclay loads, assembly of particle stacks might alter the dispersed nanoparticles and the nanoclay particles would lose their maximum efficiency in improving the modulus of the matrix, whereas even more tensile strength is obtained.

Among the nanocomposite samples, VE5 showed the best mechanical, thermal, and corrosion resistance properties. Therefore, in addition to the pure vinyl ester resin, a mixture of vinyl ester resin with 5% nanoclay was employed to prepare the carbon fiber-reinforced composites so that even further improvement in mechanical properties could be achieved. The effect of electron beam irradiation on the mechanical properties of pristine polymer (VE), selected nanocomposite (VE5), and carbon fiber-reinforced samples (VF and VFC) was also examined.

Figures 6 and 7 illustrate the effect of irradiation on the mechanical properties of VE and VE5 samples. An initial

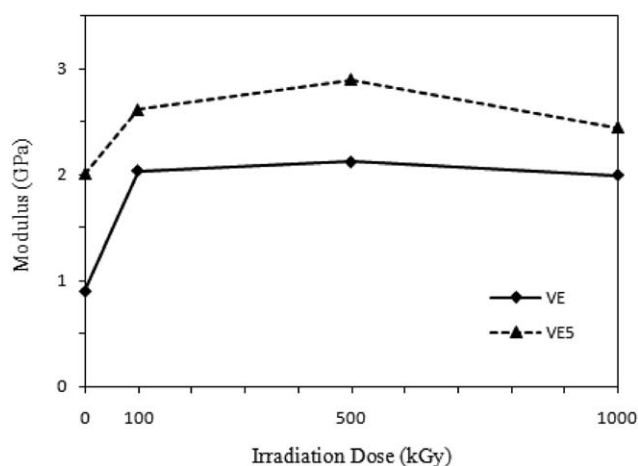


Figure 7. Effect of electron beam irradiation on tensile modulus of VE and VE5 samples.

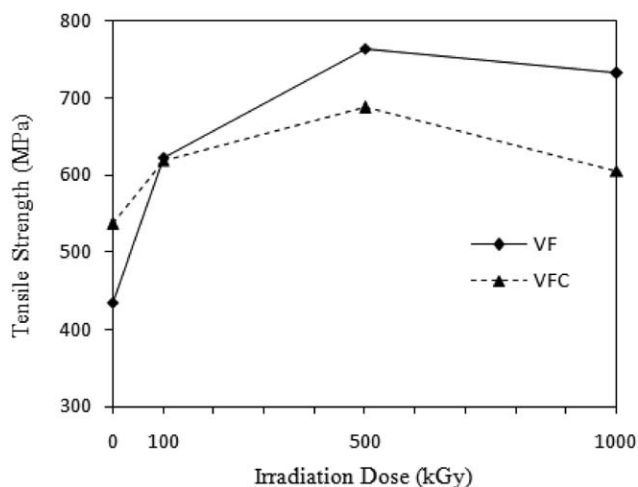


Figure 8. Effect of electron beam irradiation on tensile strength of carbon fiber-reinforced composites.

increase is observable in both tensile strengths and modulus of samples for radiation doses up to 500 kGy, followed by a decrease at higher dose (1000 kGy). That increase in tensile properties for those initial doses was caused by the intermolecular cross-linking induced by electron beam. However, at the higher studied radiation dose (1000 kGy), the chain-scissioning reactions in polymeric matrix dominated the cross-linking reactions and the mechanical properties deteriorated. The same trend is reported by Shahrajabian *et al.*¹⁶

The incorporation of carbon fiber intensely ameliorated the mechanical properties of the vinyl ester matrix (Figures 8 and 9). For example, the tensile strength of the pure vinyl ester polymer was increased from 13 to 435 MPa after reinforcement by carbon fiber. In addition, composite samples with vinyl ester/nanoclay matrix showed better properties in comparison to the samples with the pure vinyl ester matrix. The tensile strength and tensile modulus of both VF and VFC samples increased as irradiation doses rose, up to 500 kGy. At 500 kGy, the tensile strength of the composites showed the maximum values of 764 and 687 MPa for VF and VFC samples, respectively.

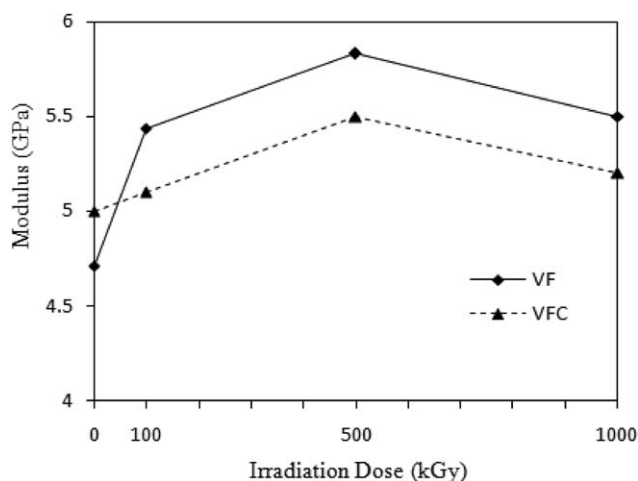


Figure 9. Effect of electron beam irradiation on tensile modulus of carbon fiber-reinforced composites.

The presence of nanoclay in the composite structure had a significant effect on the radiation-induced changes in mechanical properties. That effect is observable in vinyl ester/nanoclay composites (Figures 6 and 7) and in the carbon fiber-reinforced sample (Figures 8 and 9). However, the effect is more obvious in the samples with carbon fiber. The major initial changes in the tensile strength and tensile modulus of pure vinyl ester matrix due to the irradiation were moderated to minor changes for the samples containing nanoclay. It seems that the intense cross-linking reactions that had been evidently caused by electron beam irradiation up to 100 kGy were partially intercepted by nanoclay particles and despite the nonirradiated samples, irradiated VFC samples showed lower tensile strength in comparison to the irradiated VF samples.

Nanoclay could moderate the effect of irradiation on the polymeric matrix. The crystal structure of nanoclay has high enough resistance to bear high irradiation doses without any significant structural change.^{17,18} Exfoliated nanoclay can work as a barrier which inhibits the diffusion of oxygen into the polymeric matrix. Thus, degradation via oxidation will be retarded. At the same time, cross-linking induced by free radicals also will be reduced by the barrier effect.¹⁹

On the other hand, Hofmann degradation of the organoclay modification agent could affect the properties. Alkyl ammonium ions can undergo the Hofmann reaction, which will generate ammonium ions, acidic sites in the aluminosilicates, and the corresponding olefin. The acidic sites can lead to the formation of free radicals via accepting single electrons from donor molecules with low ionization potential. The process will result in two opposite consequences, accelerating the oxidation degradation of the polymer at the low irradiation doses (lower than critical dose), or promoting the cross-linking reactions at the high irradiation doses (higher than critical dose).²⁰

After 100 kGy irradiation, the cross-linking reactions in the polymeric matrix seem to be reduced by the barrier effect of nanoclay particles and the Hofmann reactions which increase the degradation of the polymer chains. However, the effect of mentioned factors (particularly Hofmann reactions) was moderated at higher irradiation doses. A similar trend is reported for epoxy/nanoclay composites.²¹ Despite the fact that the critical dose of the Hofmann reaction in our system is not evaluated, the effect of irradiation on the system via degradation of the surface modifier of the used nanoclay is predictable.

CONCLUSIONS

In this study, various properties of vinyl ester/clay nanocomposites were investigated. The SEM and XRD results proved that the nanoclay formed exfoliated structure for the samples containing 1, 3, and 5% of nanoclay. Thermal resistance properties of nanocomposites were increased with an increase in nanoclay content. The same trend was observed for water barrier properties of the specimens. Tafel plots showed the increase of chemical resistance of the polymer against the acidic environments after incorporation of nanoclay. Additionally, the effect of nano-

clay on the improvement of mechanical properties of the polymer was proved via tensile testing method.

According to the conducted tests, VE5 nanocomposite samples showed the best thermal, chemical, physical, and mechanical properties. Thus, the very VE5 material was used as the matrix to prepare the carbon fiber-reinforced composite. In this step, the effect of nanoclay incorporation on the mechanical properties of both pristine vinyl ester and vinyl ester/carbon fiber composite, after exposure to the electron beam irradiation was explored. Irradiation up to 500 kGy increased the tensile strength and the modulus of the samples. However, a decrease was observed as the irradiation dose rose to 1000 kGy. As far as we are concerned, nanoclay particles decreased the effects of electron beam on the specimens since the radiation-induced changes in mechanical properties were minor for the carbon fiber-reinforced vinyl ester specimens containing nanoclay.

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