RESEARCH ARTICLE

Toughening of vinyl ester resins by two-dimensional MXene nanosheets

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Abstract Two-dimensional nanosheets are highly effective tougheners for vinyl ester resins. The toughening effect is related to the high specific surface area and unique two-dimensional planar structure of the nanosheets. In this study, a coupling agent γ-(2,3-epoxypropoxy) propytrimethoxysilane (Kh-560) was used to modify MXene nanosheets (M-MXene) for use in toughening vinyl ester resin. The mechanical properties, including the tensile strength, flexural strength, Young's modulus and elongation, of neat vinyl ester resin and vinyl ester resin modified with MXene and M-MXene were investigated. The results showed that modification significantly improved the mechanical properties of the vinyl ester resin. The tensile and flexural strengths of the MXene-nanosheet-modified vinyl ester resin were 27.20% and 25.32% higher, respectively, than those of the neat vinyl ester resin. The coupling agent improved the interfacial compatibility between the MXene nanosheets and vinyl ester resin, which resulted in the tensile and flexural strengths of the M-MXene-nanosheet-modified vinyl ester resin being 52.57% and 54.60% higher, respectively, than those of the neat vinyl ester resin for a loading quantity of nanosheets of only 0.04 wt %, which is economically viable. The main mechanisms by which the nanosheets toughen the resin are crack deflection and crack pinning.

Keywords MXene nanosheets, 2D material, vinyl ester resin, modification, coupling agent

1 Introduction

Bisphenol-A-type vinyl ester resin (VER) is a

thermosetting resin synthesized by the reaction of methacrylate acid and bisphenol-A epoxy resin [1]. Compared to epoxy resin, VER has comparable mechanical properties but can be cured more quickly at room temperature, which is extremely useful [2,3]. VER is an unsaturated polyester resin that is widely applied in automobiles, marine applications, storage equipment, construction, etc. [4]. Good mechanical properties (in particular, high tensile and flexural strengths) for VER are required to enable application to the construction or manufacturing of resin matrix composites. Improving the mechanical properties of VER can considerably expand the application performance and application scope. Elastomeric tougheners, such as rubber [5,6], copolymers [7,8] and polyurethane [9], have been reported to toughen VER. Elastomeric tougheners can effectively increase the fracture toughness of resins but do not eliminate all defects. The introduction of elastomeric tougheners decreases the modulus and glass transition temperature [8] of resins, making processing more difficult.

Modification with inorganic nanoparticles is another way of improving the mechanical strength of resin [10,11]. Resins toughened with rigid inorganic nanofillers exhibit a higher modulus and impact resistance than resins modified with rubber or copolymers [12]. The effectiveness of nanofillers in toughening resins is related to several factors, such as the loading quantity, shape, size and dispersion performance of the nanoparticles. Compared to traditional inorganic nanoparticles, such as TiO_2 [13,14] and Al_2O_3 [15], 2D inorganic nanosheets can modify a resin more effectively at a low loading level due to a high specific surface area and a unique 2D structure [16,17]. Exfoliated graphene was previously found to enhanced the tensile strength of epoxy by up to 2.3 times, which was considerably higher than the 1.2-times-enhancement obtained using nanoparticles and nanoclay additives [18]. In addition, flaky graphene oxide

(GO) and its functionalized derivatives have been successfully used in several studies for toughening unsaturated polyesters [19], epoxy resins [20] and VER [21].

In this study, bisphenol-A-type VER is modified by MXene, a 2D inorganic nanosheet consisting of transition metal carbide nitrides or carbonitrides with several atomic layer thicknesses, in which large quantities of hydroxyl functional groups or terminal oxygen and fluorine are attached to the nanosheet surface [22,23]. The mechanical properties of the modified resin are tested, and an in-depth study is performed on how the MXene loading quantity affects the toughening of VER. Five samples of VER modified with MXene nanosheets at loading quantities of 0.016 wt %, 0.024 wt %, 0.032 wt %, 0.040 wt % and 0.048 wt % are investigated. Moreover, a silane coupling agent Kh-560 is used to modify the surfaces of MXene nanosheets to improve the interfacial compatibility between the resin and MXene nanosheets [24]. The coupling agent has an amphiphilic molecular structure, whereby the functional group at one end of the molecule can connect to organic substances (such as resin and rubber) and the functional group at the other end can interact with specific groups on the surface of inorganic particles [25,26]. The active hydroxyl functional groups on the surface of MXene nanosheets hydrolyzed with Kh-560 to form Si–O bonds, whereby the MXene nanosheets modified with the coupling agent (M-MXene) exhibits enhanced interfacial compatibility with VER. The coupling agent effectively bridges the inorganic M-MXene nanosheets and the organic VER.

All the results of this study show that incorporation of MXene nanosheets significantly toughens VER and the introduction of Kh-560 further enhances the mechanical properties of the modified resin. For the resins modified by MXene nanosheets, the best mechanical properties are obtained for a mass fraction of MXene of 0.04 wt % (the tensile and flexural strengths of the resin increase by 27.20% and 25.32%, respectively). For resins simultaneously modified with MXene and Kh-560, the best mechanical properties are also obtained for an MXene mass fraction 0.04 wt % (the tensile and flexural strengths of the resin increase by 52.57% and 54.60%, respectively). The toughening mechanism and the role and limitations of the coupling agent for MXene-nanosheet-modified VER are studied through fractography analysis using SEM. Existing problems and potential solutions for the process of modifying VER with MXene are discussed.

2 Experimental

2.1 Materials

Standard bisphenol-A VER (LH-884), 2-butanone peroxide (LH-V788, 45 wt % in 2,2,4-trimethyl-1,3-pentanediol diisobutyrate), and 2-ethylhexanoate (LH-836JCB-1) were obtained from the Qingyuan Meiheng New Material Technology Co. γ-(2,3-Epoxypropoxy) propytrimethoxysilane (Kh-560) was purchased from Sigma-Aldrich. Absolute ethanol (99.5% ethanol), LiF and HCl were purchased from Aladdin. Ti_3AlC_2 MAX powder (~40 μm) was purchased from the Zhongxin New Materials Co., China. Deionized water (with a resistivity of 18 MΩ·cm) was produced in the laboratory.

2.2 Synthesis of the MXene nanosheets

Detailed synthesis of the MXene nanosheets solution can be found in our previous work [27–30]. Briefly, 4 g of Ti_3AlC_2 MAX were added to a premixed etchant solution with 4 g of LiF and 40 mL HCl solution under magnetic stirring. The mixture was maintained at 35 °C and allowed to react for 24 h under stirring. The $Ti_3C_2T_x$ slurry product was washed with deionized water until a pH of 6 was reached. The final product was obtained by sonicating the $Ti_3C_2T_x$ slurry in deionized water for 1 h under an argon flow, followed by centrifugation at 3500 r·min^{-1} for 1 h. This simple preparation process of the MXene nanosheet solution is shown in Fig. 1.

2.3 Synthesis of the modified MXene nanosheets

To effectively disperse the MXene nanosheets in VER, the deionized water in the MXene dispersion was replaced with an ethanol solution. Kh-560 was mixed with ethanol in a 1:10 ratio under 30 min of sonication, followed by the addition of a prescribed quantity of the MXene ethanol dispersion. The intermediate product was maintained at 70 °C and stirred for 1 h, followed by 20–30 min of sonication. The thus prepared M-MXene dispersion was stored for future use.

2.4 Preparation of nanosheets/resin composite

MXene-based resin nanocomposites were prepared via similar procedures. Generally, the resin (5 g) was mixed with the MXene/M-MXene dispersion solution (at five different loading quantities of 0.016 wt %, 0.024 wt %, 0.032 wt %, 0.040 wt %, and 0.048 wt %) in a flask under magnetic stirring for 1 h, followed by sonication in a bath for 30 min to evenly disperse the MXene/M-MXene. The resin dispersion solution was heated to 80 °C to evaporate the ethanol. Then, 1 wt % (≈ 0.05 g) of 2-ethylhexanoate was added to the dispersion as an accelerator promoter for the reaction, followed by stirring for 10 min. The resin dispersion solution was subsequently initiated with 1 wt % (≈ 0.05 g) of 2-butanone peroxide and reacted for 10 min under magnetic stirring, followed by degassing in vacuum for 20 min. The resin was then poured into a homemade silicone mold, followed by curing at room temperature for
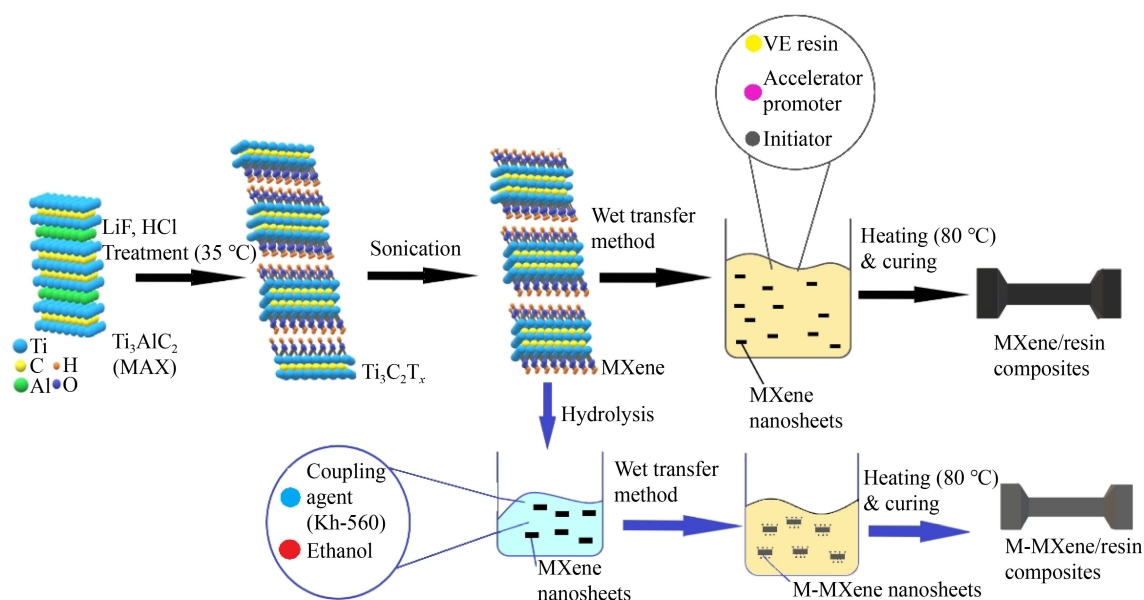
Fig. 1 Preparation process of the MXene nanosheets and nanosheets/resin composites.

24 h and at 80 °C for 2 h. All the samples were cut into test specimens.

2.5 Characterization

Infrared spectroscopy (IR) was performed with FTIR–ATR on the neat VER and MXene-modified VER flakes using a Fourier transform infrared spectrometer (FTIR). The fracture toughness of the neat resin and modified VER was determined using an INSRON-5967 double column system according to GB/T Standard 2567-2008. All the specimens were preformed into rectangular shapes, with a length of 200.0 ± 0.2 mm, width of 100 ± 0.2 mm, and thickness of 3.5–4.5 mm. All the specimens were pulled at a speed of 10 mm·min^{-1} until completely broken. The flexural strength and flexural modulus of the corresponding VER nanocomposites were tested using the three-point bending method. A JEOL 6700 field emission electron microscope (SEM) was used to determine the toughening mechanisms. The fractured tension specimens were attached to a sample holder using conductive tape. The SEM samples were coated with a thin platinum layer to increase the conductivity. SEM images were taken at an accelerating voltage of 10 kV.

3 Results and discussion

3.1 Structure analysis

This section is an analysis of the microstructure and chemical and mechanical properties of the MXene nanosheets and nanosheet/resin composites. Figure 2 shows SEM images of the prepared MXene nanosheets. The excellent toughening effect of the MXene nanosheets
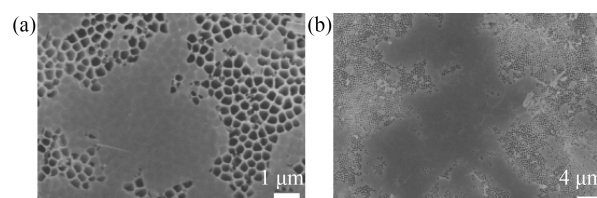

Fig. 2 SEM images of (a) the MXene nanosheets in low magnification and (b) the MXene nanosheets in high magnification.

can be attributed to their planar structure and ultrahigh aspect ratio. However, untreated MXene nanosheets tend to aggregate and stack, which reduces the modification effect for VER. Thus, the nanosheets and the MXene nanosheets/resin composites were sonicated to increase dispersibility.

A comparative analysis of the unmodified MXene nanosheets and Kh-560-modified MXene (M-MXene) nanosheets is performed. EDXS results for the elemental distribution of both types of nanosheets are shown in Fig. 3. The elemental distributions of C and F show the MXene nanosheets are homogeneous. The presence of elemental Si in the coupling agent Kh-560 can be clearly observed in the mapping result for the M-MXene nanosheets, whereas there is almost no elemental Si in the MXene nanosheets, indicating that the modification procedure was successful. Elemental silicon originated from the terminal functional groups of the M-MXene nanosheets after treatment with the Si-containing coupling agent Kh-560 via a hydrolysis step.

FTIR–ATR analysis was performed to evaluate the chemical structure of the MXene and M-MXene nanosheets. In Fig. 4, the main peaks at 3570 and 565 cm^{-1} correspond to the hydroxyl and Ti–O groups of the MXene and M-MXene structures, respectively. Compared
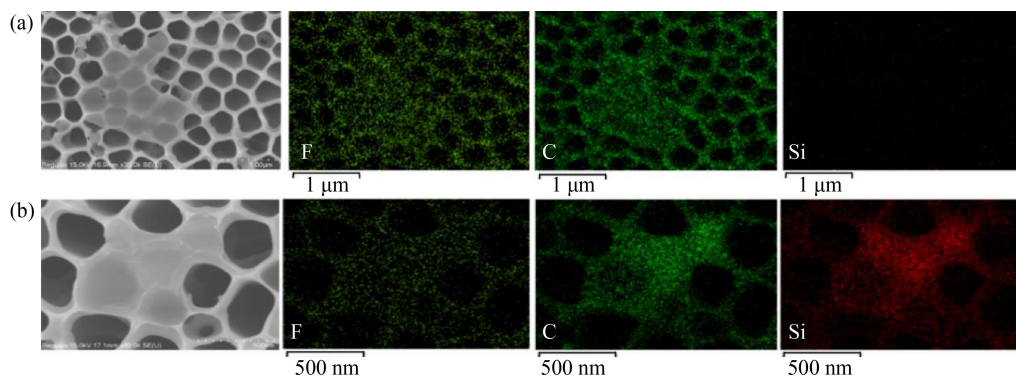
Fig. 3 The SEM images and elemental distribution results of (a) the MXene nanosheets and (b) the M-MXene nanosheets.
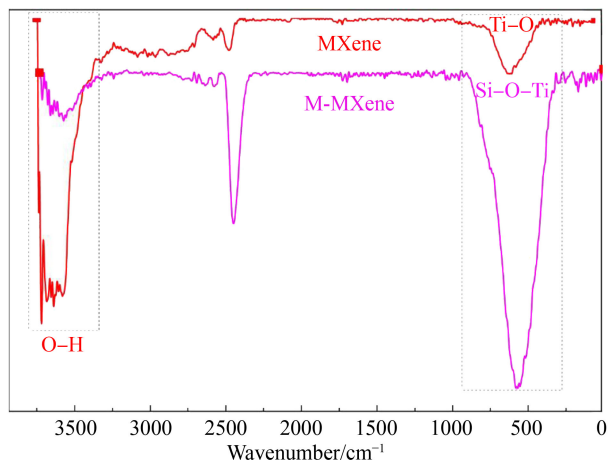

Fig. 4 Infrared spectra results of the MXene and M-MXene nanosheets.

to the spectrum of the MXene nanosheets, the absorption band from the O–H stretching vibration in the spectrum of M-MXene nanosheets is considerably weaker in intensity because the reaction between MXene and ethanol results in dehydration of the –OH groups of MXene and Kh-560. The strong peak in the range of 960–303 cm^{-1} in the spectrum of the M-MXene nanosheets can be considered as the superposition of two peaks, one from the deformation vibration of the Ti–O bond and one from the stretching vibration of Si–O–Ti [31], indicating the MXene nanosheets were successfully modified by the coupling agent Kh-560.

3.2 Mechanical properties of the MXene/M-MXene modified VER composites

Figure 5 shows the tensile toughness of the different VER nanocomposites. The tensile toughness of both the MXene/VER and M-MXene/VER composites clearly increases with the loading quantity of the MXene/M-MXene nanosheets in the ultralow loading range. The increase in the tensile toughness of the modified VER compared to that of VER reaches a maximum at approximately 27.3% and 52.6% at 0.04 wt % loading of MXene and M-MXene, respectively; that is, the tensile

strength increases from 70.0 MPa for VER to 89.1 MPa and 106.8 MPa for VER modified with MXene and M-MXene nanosheets, respectively. The incorporation of MXene nanosheets into VER clearly improves the mechanical properties of the resin. This result may be related to the effect of the nanosheets on the fracture mechanism and crack development process. The tensile toughness of the VER composites decreases at an excessive loading quantity (above 0.048 wt %). This result is related to the dispersion of the MXene nanosheets in resin and the self-agglomeration of the nanosheets. These results show that the introduction of MXene nanosheets can enhance the mechanical properties of the resin. Modification of the MXene nanosheets by the coupling agent further enhances the mechanical properties of the resin by 25.3% for a 0.04 wt % loading of M-MXene. The mechanism by which M-MXene further enhances the mechanical properties of the resin is that the Si–O functional groups attached to the surface of M-MXene nanosheets combine with the carbon in the resin through a hydrolysis reaction to form Si–O–C bonds. The interfacial crosslinking characteristics between the resin and nanosheets are improved. The tensile modulus results presented in Fig. 6 show that the strength modulus of the MXene/VER nanocomposites is almost maintained (corresponding to only a slight increase) because of the incorporation of an ultralow quantity of MXene/M-MXene nanosheets, which is in accordance with the trend reported for modified graphene oxide containing unsaturated polyester and VER [32].

Figure 7 shows the flexural strength and flexural modulus of the MXene/M-MXene-modified VER composites. The flexural strength of the resin composites increases with the loading quantity of the MXene or modified MXene nanosheets, showing a similar trend to that for the tensile strength. The flexural strength of VER increases by 25% and 54% upon incorporation of MXene and M-MXene nanosheets, respectively, at a loading quantity of 0.04 wt % because the interfacial compatibility increases, whereas there is only a slight increase in the flexural modulus of the nanosheets/VER nanocomposites over that of VER.
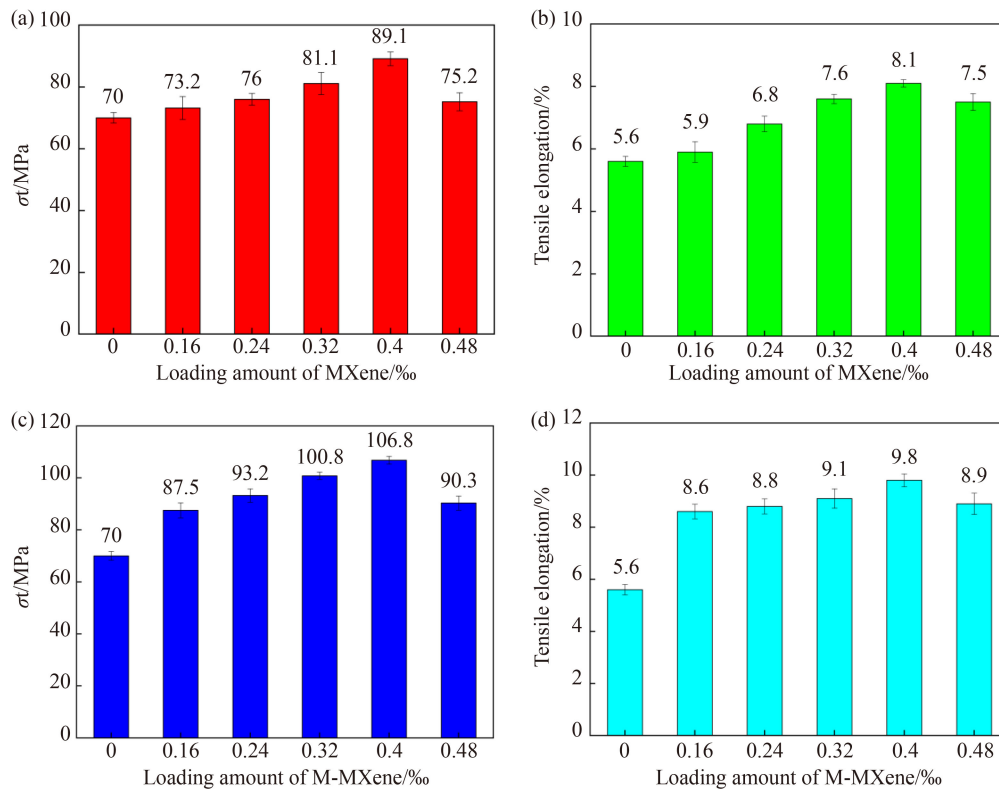
Fig. 5 Tensile toughness (σt) of the MXene/M-MXene modified VER composites. (a) Tensile strength and (b) tensile elongation for the MXene modified VER composites, (c) tensile strength and (d) tensile elongation for the M-MXene modified VER composites.
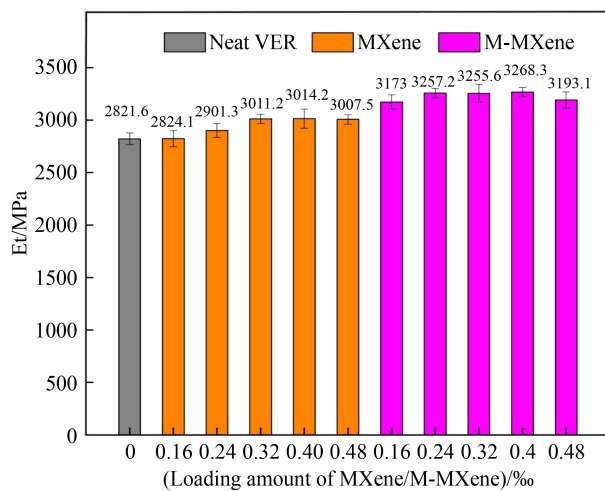

Fig. 6 Tensile modulus (Et) of the MXene/M-MXene modified VER composites.

3.3 Fractography analysis

Representative SEM images are shown for failed compact tension samples of neat VER (Fig. 8) and MXene- and M-MXene-modified VER composites (Fig. 9). The fracture surface of the neat VER is very smooth and flat, and several parallel fine lines are distributed throughout the surface. This result shows that neat VER has relatively low mechanical properties and is brittle. By

contrast, toughening events are observed for the MXene/M-MXene-modified VER composites, including crack pinning, crack deflection, and debonding of nanosheets [33]. River-like cracks and tadpole-shaped "bright tails" can be observed on the fracture surfaces of the MXene-modified VER shown in Fig. 9(a), which mostly result from crack pinning and crack deflection [34]. As the loading quantity of MXene nanosheets increases, the number of cracks per unit area generally increases, and the fracture surfaces exhibit layered cracks (Fig. 9(c)), irregular cracks and microholes (Figs. 9(e) and 9(g)).

The MXene-modified VER composites exhibit plastic deformation features, such as irregular surface textures, which shows the loading quantity of MXene nanosheets is related to the resin toughness [35]. Figure 9(i) shows the fracture features of VER composites containing an excessive quantity of MXene nanosheets, which are similar to those observed in Fig. 8. The M-MXene-modified VER composites exhibit analogous fracture features to those of the MXene-modified VER composites. However, more river-like cracks can be observed in Figs. 9(b) and 9(d) than in Fig. 8 because of the enhanced interfacial adhesion between the modified MXene nanosheets and the resin. VER modified with 0.04 wt % M-MXene exhibits apparent plastic deformation characteristics, such as stepped blunt edges and irregular cracks. Figure 9 shows the toughening
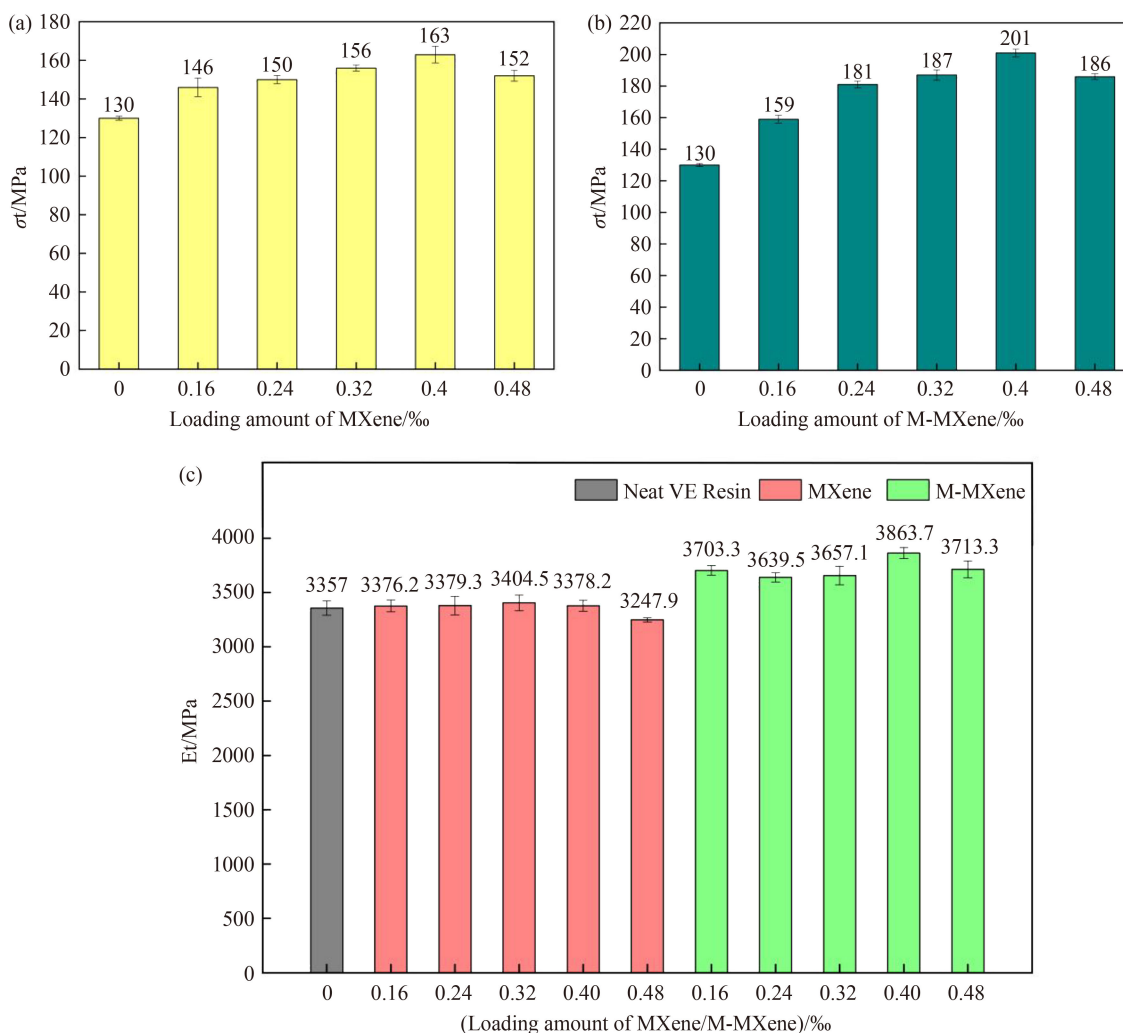
Fig. 7 Flexural strength of (a) the MXene modified VER composites and (b) the M-MXene modified VER composites and (c) flexural modulus of the MXene/M-MXene modified VER composites.
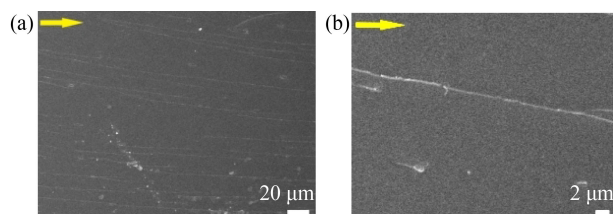

Fig. 8 Representative SEM image of the failed compact tension sample of the neat VER (a) in low magnification and (b) in high magnification. Yellow arrow indicates the direction that crack propagates.

mechanism for the resin by the MXene nanosheets is the same as for the M-MXene nanosheets. More cracks are observed in the fractographs of the resin samples modified with M-MXene than those modified with MXene.

A fractography analysis shows that crack pinning and crack deflection (see Fig. 10) are the major mechanisms by which the MXene nanosheets toughen VER. The rough, river-like cracks and fracture surface with tadpole-shaped features observed in Fig. 9 are consistent with these mechanisms. The nanosheets block crack propagation, forcing the crack to go around the nanosheets and form an edge after crack pinning. In addition, the crack path is deflected when a crack encounters a nanosheet, such that irregular crack edges are left around the nanosheets. Furthermore, debonding features and microholes can be observed, which also contribute to the toughness.

4 Conclusions

In this study, MXene nanosheets are used to modify VER, and the 2D nanosheet/resin composites exhibit superior fracture toughness without a significant reduction in the elastic modulus compared to VER. Moreover, MXene nanosheets functionalized with the coupling agent Kh-560 (M-MXene) can further toughen VER because the coupling agent enhances the interfacial
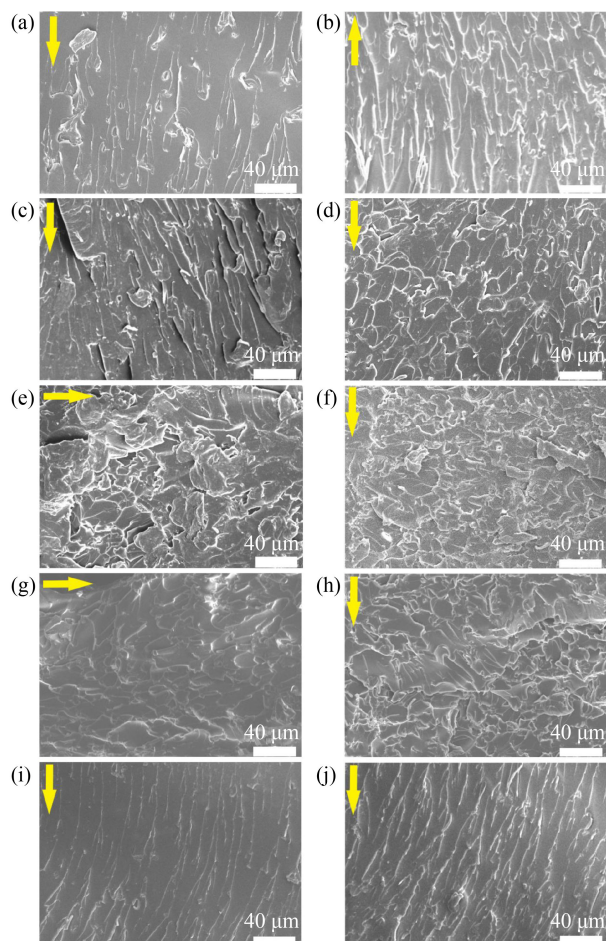
Fig. 9 Representative SEM images of the failed compact tension samples of the MXene modified resin samples with loading amount of (a) 0.016 wt %, (c) 0.024 wt %, (e) 0.032 wt %, (g) 0.040 wt %, (i) 0.048 wt % and M-MXene modified resin samples with loading amount of (b) 0.016 wt %, (d) 0.024 wt %, (f) 0.032 wt %, (h) 0.040 wt %, (j) 0.048 wt %. Yellow arrows indicate the direction that crack propagates.
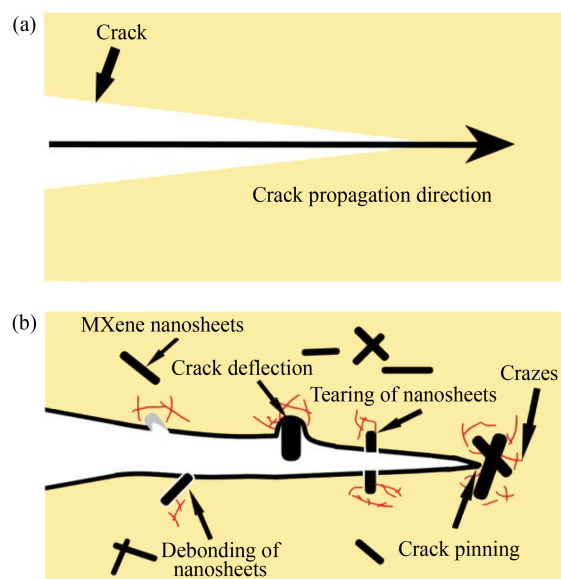

Fig. 10 A brief schematic of possible mechanism that MXene nanosheets toughens VER. (a) crack propagation path of neat VER; (b) crack propagation path of MXene nanosheets modified VER.

compatibility between MXene and VER. When the loading quantity of nanosheets is 0.040 wt %, the mechanical strength of the modified resin reaches a maximum, where the tensile and flexural strengths are 89.1 MPa and 162.9 MPa, respectively, for MXene-modified VER and 106.8 MPa and 201.54 MPa, respectively, for M-MXene-modified VER. Crack pinning and crack deflection are found to be the main toughening mechanisms in VER modified with MXene and M-MXene. As the loading quantity of nanosheets increases, additional plastic deformation features, such as craze and microholes, are observed. This study provides a strategy for improving the mechanical properties of VER, while paving the way for the application of novel materials, such as 2D nanosheets, to the resin modification field.

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