FINITE ELEMENT SIMULATION OF MECHANICAL PROPERTIES OF NOVEL POLYMER COMPOSITES REINFORCED WITH MXENE NANOSHEETS

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Abstract
Two-dimensional (2D) nanomaterials such as graphene, transition metal oxides, metal oxides, metal hydroxides and others are currently amongst the most intensively studied classes of materials that hold great promise for future applications in many technological areas. Graphene is by far the best known and the most studied 2D nanomaterial. Recently discovered a new family of 2D nanomaterials MXenes shows similar benefits for structural composites as graphene. An exploration of this new class of material is still in an initial stage and opportunities of MXenes as fillers for nano-engineered structural polymer composite are not fully identified and exploited. The aim of this study is to identify the suitable finite element modelling methodology in support of the mechanical properties optimization for polymer composite reinforced with two types of 2D nanoparticles: MXene and graphene. In order to carry out numerical study of mechanical properties relationship upon MXene/graphene based polymer composite microstructure, three dimensional finite element models were selected. It was chosen 2D nanoparticles be randomly distributed in polymer matrix and as a very important aspect of modelling the MXene/polymer and graphene/polymer matrix interfaces was taken into account.

1. Introduction

The new 2D nanomaterials MXenes were discovered in 2011. They were produced by the extraction of the A-group layers from the transition metal carbides and/or nitrides, known as the MAX phases [1]. Although ternary carbides and nitrides after mechanical deformation can be formed into lamellas, the thicknesses of them varies from tens to hundreds nanometres [2]. While MXenes can be exfoliated into few nanometres sheets similar to the graphene.

Till now graphene attracts more attention than all other 2D materials together. The main advantages of graphene are excellent conductive and mechanical properties. Graphene is used in a wide range of application including light weight, high strength polymer composite materials [3, 4]. Graphene was discovered in 2004 but the commercial use of graphene is still limited due to expensive suitable for industry methods and some disadvantages [5]. In particular, graphene has hydrophobic surface resulting in agglomeration, poor compatibility and dispersibility in polymers, weak interfaces and insufficient mechanical reinforcement effect [6]. This turns for searching of the next evolutionary step in materials development providing solutions for the “beyond graphene” era, needed to meet the challenges of global competition.

Theoretically, MXenes possess high in-plane Young’s modulus and strength, traditionally associated with early transition metal carbides, combined with thermal stability and electrical conductivity [1, 7]. While MXenes’ strength and stiffness are lower than that of graphene, their bending rigidities should be much higher for Ti_2C, Ti_3C_2 and Ti_4C_3 MXenes as predicted by molecular dynamics calculations [8, 9]. These attributes render MXenes attractive 2D materials to reinforce polymers for a vast array of applications. 2D nanomaterials can be divided into two groups: hydrophilic but not conductive, such as transition metal oxides, clays; or conductive, but not hydrophilic, such as graphene. MXenes may be able to impart high electrical conductivity together with excellent mechanical properties. While they conduct heat and electricity like metals, they are elastically stiff, strong, brittle, and heat-tolerant like ceramics [1, 10]. They are resistant to chemical attack, readily machinable, and thermal shock, damage tolerant, and fatigue, creep and oxidation resistant [11].

The exploration of MXenes is still in a nascent stage but challenges and opportunities of this 2D materials as fillers for nano-engineered structural polymer composite are not fully identified and exploited. Despite on relatively easy processing technology, yet MXenes are synthesized in limited amounts and cannot satisfy the growing quantitative demands for their scientific and technological applications. Development of hybrid polymer composites by combination of MXenes with graphene is an opportunity to fully exploit potential of novel nanoparticles at the early stage of their discovery.

Here, the analysis of the use of finite element (FE) methods possibilities for the microstructural modelling of mechanical properties of polymer composites reinforced with novel MXene nanosheets and graphene is presented. The aim of this study is to identify the suitable FE modelling methodology in support of the mechanical properties optimization for MXene/graphene based polymer composites.

2. Materials

As it is intent to develop the new hybrid material for nano-engineered structural polymer composite the MXene/graphene/epoxy polymer composite is analysed. The epoxy resin as a matrix of composite with graphene was under interest in a plenty of studies but as far as it is known never with MXene nanosheets. MXenes were used as fillers only for polydiallyldimethylammonium chloride (PDDA) and polyvinyl alcohol (PVA) [10]. From the large family of epoxy resins here it is chosen the one with Young’s modulus of 2.13 GPa; tensile strength of 50 MPa [12]. For finite element modelling it is needed not only to define various materials properties but the shape and dimensions of nanoparticles as well. Table 1 shows an overview of mechanical and dimensional properties of MXenes and graphene presented in literature.

It should be noted that the chosen nanofillers differ in size. The thinnest MXenes with n = 1 in $M_{n+1}X_n$ formula can be less than one nanometre. For more complex MXenes the thickness can be higher and equal to a few nanometres. So, MXenes are at least 2-3 times thicker than graphene. It was not possible to find an information about the aspect ratio of MXene particles but for initial modelling some assumptions can be made, for instance, it could be accepted that it is the same or similar as this of graphene.

Table 1. Properties of 2D nanosheets

Material property	2D nanoparticle	
	Graphene	MXene
Thickness of nanosheet, nm	0.335 [13, 14]	~1-3 [1, 10, 11, 15]
Aspect ratio	1-114×10^3 [16, 23]	-
Diameter of nanosheet, µm	10-40 [16, 23]	-
Young's modulus, TPa	0.799-1.110 [13, 17, 18]	0.597 [8], 0.636 [11] (Ti_2C) 0.502 [8], 0.523[11] (Ti_3C_2) 0.534 [8], 0.512 [11] (Ti_4C_3) 0.718 [11] (V_2C) 0.690 [11] (Cr_2C) 0.788 [11] (Ta_2C) ~0.500 [7] (various)
Poisson's ratio	0.149-0.450 [18, 20]	0.23 [19] (Ti_2C)
Tensile strength, GPa	120-130 [13, 17]	32-37 [8] (Ti_2C) 19-24 [8] (Ti_3C_2) 24-28 [8] (Ti_4C_3)
Failure strain, %	20 [17]	5-8 [8], 17-18 [28] (Ti_2C) 3-6 [8], (Ti_3C_2) 6-9 [8], (Ti_4C_3)
Bending rigidity, eV	2.3 [21, 22]	5.21 [9] (Ti_2C) 49.55 [9] (Ti_3C_2) 47.43 [9] (Ti_4C_3)

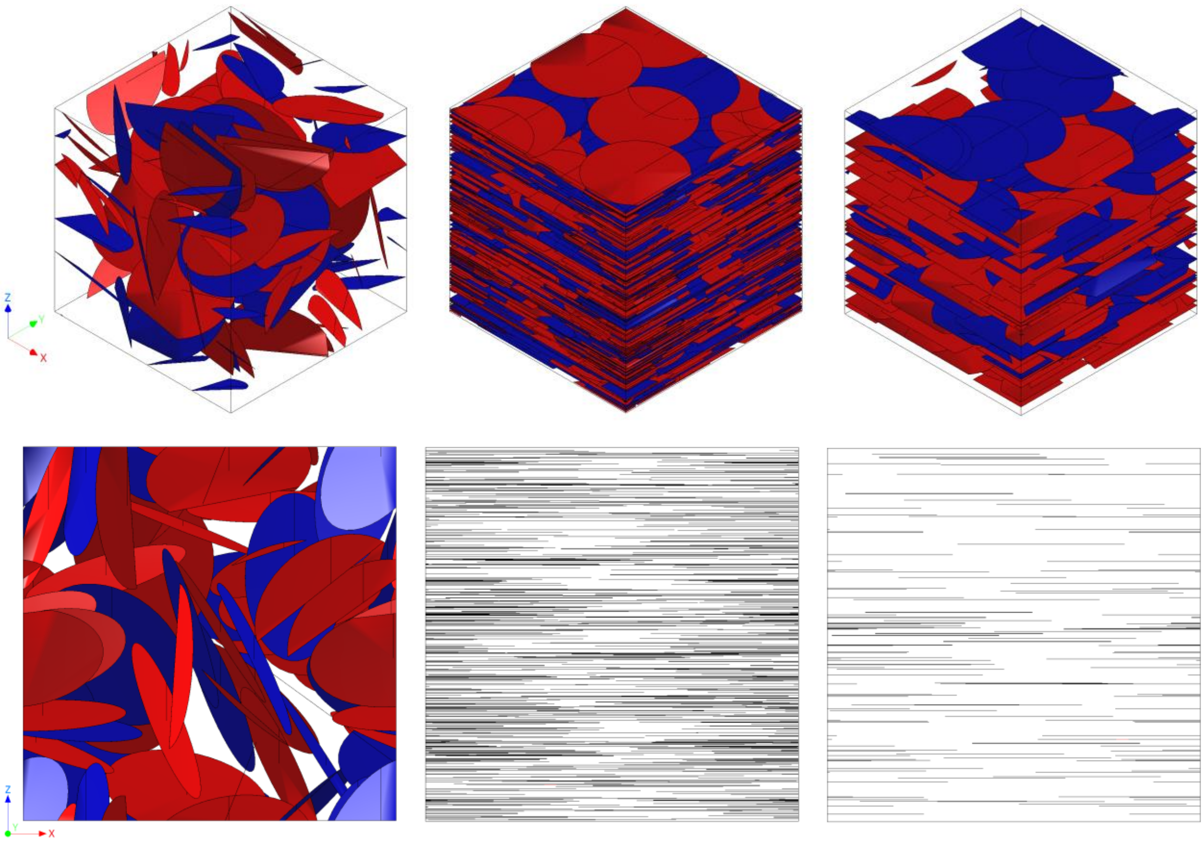
If the mechanical properties of graphene nanolayer were not only calculated but checked experimentally as well; these of MXenes were only predicted by simulation of classical molecular dynamics. Different studies present Young's modulus of graphene varying from 0.799-1.110 TPa, but the most common case is when modulus of graphene is defined as 1 TPa. This is double to compare with MXenes one. Again, as up to date it is known about 20 different MXenes, the modulus of it depends on the particular material and a minimum value obtained is 0.5 TPa, maximum 0.788 TPa (Ta_2C) . Poisson's ratio for both graphene and MXenes can be defined by the similar value. From the Table 1 it can be seen that MXenes show lower tensile strength. According to different approaches the failure strain of MXenes varies in a wide range. The bending rigidity of MXene nanosheet is significantly higher because of the higher thickness of nanosheet.

Nanofiller/polymer matrix interfaces have a significant influence on the mechanical properties and strength of nanocomposites [16]. The mechanical properties of graphene/epoxy matrix interfaces were diligently investigated using so called inverse modeling [16, 24-27]. In these studies, it is noted that the extraordinary effect of nanoreinforcement on the mechanical properties of nanocomposites is related with the interaction between the nanoreinforcements and polymer matrix, leading to the formation of a polymer layer with modified, perturbed chain structure [25]. Taking into account the relatively poor adhesion between the graphene and polymer layers, it was demonstrated that the elastic modulus of the graphene/polymer interface is 1.76 times higher than that of pure polymer. For the graphene/epoxy interface it was used Young modulus 3.74 GPa ($2.13 \times 1.76 = 3.74$) and strength 32.4 MPa. The thickness of the interface layer was of 1 nm [16].

According to the presented methodologic [16, 24-27] the mechanical properties of MXene/epoxy matrix interface could be predicted. It is expected that the great difference between these two nanoparticles is being of MXenes hydrophilic opposite then graphene. In this case should be taken into account a good adhesion between the MXene and polymer layers. Due to this, the elastic modulus of the MXene/polymer interface should be higher than this of graphene/epoxy matrix interface.

3. Modelling

To analyse microstructure – strength relationships of MXene/graphene/epoxy polymer composite, 3D computational microstructural models, or so called representative volume elements (RVEs) were developed. It was intended to investigate the effects of particles aspect ratio, shape, clustering, orientation, volume fraction in total and separately for different particles, on the mechanical behaviour of nanocomposite. Due to this, a number of RVEs were generated using the commercial finite element code DIGIMAT™ to ANSYS®. Some examples of microstructural models are shown in Figure 1. The presented RVEs were developed according to the literature review presented above; the following parameters were used: the diameter of each 2D nanoparticle of 10 μm; effective interface between filler and matrix of 1nm; graphene thickness of 0.34 nm, aspect ratio of 4250; MXenes thickness of 1.5 nm; aspect ratio 2860; an edge dimension of epoxy matrix cube of 22.3 μm. The target volume fraction of nanoparticles was 1.0% and 0.2% in total. The more detailed data for these RVEs generation are presented in Table 2. The numerical simulations were carried out by different 3D models subject to uniaxial tensile loading. The maximum principal stress criterion was used for the evaluation of initial defects.



a *b* *c*

Figure 1. Some of RVEs of MXene/graphene/epoxy polymer composites: random 0.1% (*a*); aligned 1% (*b*); aligned 0.2% (*c*).

Table 2. RVE models generation of MXene/graphene/epoxy polymer

2D Nanoparticle filler	Target volume fraction, %	Target inclusion quantity	Generated inclusions	Effective volume fraction, %
Graphene aligned	0.5	300	300	0.5
MXenes aligned	0.5	202	202	0.5
Graphene aligned	0.1	60	60	0.1
MXenes aligned	0.1	40	40	0.1
Graphene randomly	0.1	60	30	0.0483
MXenes randomly	0.1	40	20	0.0475

5. Conclusions

In this paper the possibilities of the investigation of microstructure – mechanical properties and strength relationships of MXene/graphene/epoxy polymer nanocomposites using 3D micromechanical unit cell models and finite element modelling are presented.

The detailed analysis of MXenes and graphene particles dimensions and mechanical properties of nanosheets was carried out based on the recent works. The comparative study showed that MXenes are at least twice thicker than graphene, have lower strength and stiffness properties, but according to early stage investigations they show high hydrophilic properties and are promising to enhance mechanical behaviour of composite through high adhesion between filler and matrix.

3D computational microstructural representative volume element models were developed and as a very important point of modelling the MXene/polymer and graphene/polymer matrix interfaces was taken into account.

The effects of 2D particles MXene and graphene aspect ratio, shape, clustering, orientation, volume fraction in total and separately for different particles, on the mechanical properties optimization of polymer composite for structural applications were analysed.

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