Numerical study on the effect of CaCO₃ ratio on the mechanical properties of CaCO₃/PVC composites

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Abstract. The effect of CaCO₃ (calcium carbonate) ratio on the mechanical properties of CaCO₃/PVC (polyvinyl chloride) composites was studied by numerical simulation in this paper. The representative volume units of CaCO₃/PVC Composites with different CaCO₃ ratios were established by using the random dropping method. The stress-strain variation of CaCO₃/PVC composites with different CaCO₃ ratios under tensile or compressive loads was calculated, and the influence of CaCO₃ ratio on the stiffness of CaCO₃/PVC composites was discussed. Considering the comprehensive effect of calcium carbonate ratio on stiffness and stress-strain, the best ratio of calcium carbonate in PVC is 25%.

1. Introduction
In the research of composite materials, CaCO₃ (calcium carbonate) powder is often used to fill the plastic matrix because of its rich resources, low price, non-toxic and tasteless characteristics, so as to improve the mechanical properties of plastics.[1-5] The proportion of CaCO₃ in CaCO₃/plastic composites is a key factor which affects the mechanical properties. Since the filling method of CaCO₃ in plastic matrix is usually random, it is difficult to accurately describe the structural mechanism of the composite formed by mixing. Therefore, it is hard to calculate and predict the mechanical properties of CaCO₃/plastic composites theoretically The related researches were usually carried out by using experimental methods. Sepeth et al.[6] prepared stearic acid modified nano CaCO₃/HDPE composite and studied its mechanical properties. Compared with pure HDPE, the tensile strength of the composite increased by 5% when the filling content was 1%, and the bending strength increased by 4.5% when the filling content was 15%. Lin et al.[7] added modified nano CaCO₃ to polypropylene, the filling amount was 20%. The experimental results showed that the tensile modulus and impact strength of the material were improved at the same time. Yang et al.[8] prepared nano-CaCO₃/polybutylene succinate composite materials. The experimental results showed that the tensile strength of the material increases from 30.39MPa before filling modification to 42.12MPa. Wu et al.[9] prepared CaCO₃/PVC composites with different proportions by using CaCO₃ particles of different sizes. The experimental results showed that the mechanical properties of PVC composites filled with ordinary light CaCO₃ and superfine light CaCO₃ were relatively good. Many scholars have improved the properties of CaCO₃/PVC composites by binder or process.[10-12] Moreover, many scholars have also studied the effect of calcium carbonate on the mechanical properties of other plastics.[13-16] Compared with pure plastics, the tensile strength, flexural strength and impact strength of CaCO₃/plastic composites are significantly improved.[17-19] However, the research methods are usually empirical research, which takes a lot of time, equipment and resources.
What’s more, it is difficult to analyze the stress-strain relationship between the filled particles and the plastic matrix through the experimental method, which is important for properties improvement.

In this paper, PVC plastics were used as the filling matrix, and representative volume elements (RVE) of CaCO$_3$/PVC composites with different mixing ratios were established from the micro (micron level) perspective. The finite element method was used to simulate the CaCO$_3$/PVC composites under certain loads, and the mechanical properties of CaCO$_3$/PVC composites under different mixing ratios were observed. The stress-strain relationship between CaCO$_3$ and PVC was calculated. The results could provide a theoretical basis for CaCO$_3$/PVC composites, which takes the properties improvement into account, and reduces the stress between different composition. In addition, the development cycle of new composite materials is reduced, with the goal for a best CaCO$_3$/PVC filling ratio.

2. Numerical model

2.1. Composition and mechanical properties

In this paper, PVC was used as the filler matrix. The related parameters of PVC were as follows: the density of 1380 kg/m$^3$, the modulus of elasticity of 6 GPa, the tensile strength and compressive strength are 50MPa, and the Poisson's ratio of 0.47. When the spherical CaCO$_3$ particle with a diameter of 1 $\mu$m was used as the filler, the relevant parameters of CaCO$_3$ were as follows: the density of 2700 kg/m$^3$, the elastic modulus of 68.8GPa, and the Poisson's ratio of 0.31.

As PVC material is the matrix in the composites, its composition accounts for the vast majority, and it is also the main part that needs to improve the mechanical properties. Therefore, this paper mainly focuses on the stress-strain changes of PVC matrix before and after CaCO$_3$ particles filling, as well as the change of tensile and compressive elastic modulus of the whole composite. According to Hooke's law, the calculation formula of elastic modulus E of elastic material is as Equ. (1).

$$E = (FL)/(\delta LS) $$  \hspace{1cm} (1)

where ‘F’ is an external force on the material along a certain direction, ‘L’ is the original length of the material in the f direction, ‘$\delta L$’ is the elongation of the material in the f direction under the external force F, and ‘S’ is the cross-sectional area of the material in the f direction.

2.2. Representative volume unit of CaCO$_3$/PVC composites

In order to accurately characterize the specific changes of a macro scale object, the micro scale of object should be considered during modeling. Generally, representative volume element (RVE) is used to construct the microstructure and properties of materials at the micro scale. RVE is the smallest volume unit. It is required that the modified volume unit contains enough geometric information, crystallographic orientation information, distribution information and phase field information of microstructure components, and can represent the basic characteristics of material microstructure in statistical sense.

Digimat is a multi-scale nonlinear composite material modeling platform, and the Digimat-FE module is applied to establish a RVE of CaCO$_3$/PVC composite in this paper. The CaCO$_3$ powder is defined as a sphere with a diameter of 1 $\mu$m. The filling method is a three-dimensional random filling method, and the boundary is a periodic boundary. The minimum distance between particles in the matrix is set to 0.05 times the particle size of CaCO$_3$, and mutual inclusion is not allowed. However, when the CaCO$_3$ ratio exceeds 25%, the CaCO$_3$ particles cannot be smoothly filled into the matrix, and the CaCO$_3$ particles in the matrix need to be allowed to exist in volume. Taking 5% as the filling ratio tolerance, the RVE models of CaCO$_3$/PVC composite are established, with the CaCO$_3$ volume fraction of 0, 5%, 10%, 15%, 20%, 25% and 30%, respectively. The RVE model is a regular hexahedron with the length of 5 $\mu$m, as shown in Fig. 1.
2.3. ANSYS Workbench static analysis
In the Static Structural module of ANSYS Workbench, the finite element simulation method is used to apply loads to RVE. From a microscopic point of view, the tension, pressure, bending moment and shearing force can be divided into two types of loading: tensile loading and compressive loading. The RVE model established by Digimat-FE is imported into ANSYS workbench, and a static analysis module is established to apply tension and pressure load. Then, the results of deformation, stress and strain are obtained.

2.3.1. Mesh
The PVC matrix and CaCO₃ particles are grouped into one part, which can realize the common interface sharing grid and node coupling. Therefore, each body can independently divide the grid and configure the material properties. The mesh is divided automatically. The number of elements in 10%-CaCO₃ RVE and 13%-CaCO₃ RVE are 59995 and 227352 respectively. And the average element quality is between 0.8 and 0.9. The division result is shown in Fig. 2 and Fig. 3 respectively.

2.3.2. Tensile loading
While applying tensile loading, the PVC matrix is ensured for undamaged. Therefore, the fixed constraint is applied on one side of the RVE, and the vertical uniform tension is applied on the other side opposite to the fixed constraint. The tensile strength is 40MPa in this study.

2.3.3. Compressive loading
Since the established RVE model adopts periodic boundaries, the CaCO₃ particles on the RVE boundary are cut, and the cut part is filled to the opposite surface (the smallest particle that exists in the boundary is 30% of CaCO₃ spheres). The pressure load is closer to reality. It is necessary to add a steel plate that is not prone to deformation (elastic modulus of 200GPa) on the upper and lower compression surfaces of the RVE as a direct pressure bearing body, and the steel plate will then evenly transmit the load to
the RVE. Assuming that the PVC matrix is not damaged, the applied compressive load is 40MPa. One of the steel plates is fixed, and a compressive loading is applied perpendicular to the upper surface of the other steel plate.

3. Results and discussion

3.1. Tensile properties

Under the tensile strength of 40MPa, the calculated results of stress, strain and deformation for 10%-CaCO3/PVC composite are displayed in Fig. 4. The overall stress of PVC matrix is small, however, there is a significant stress concentration at the position where is in contact with CaCO3. The overall stress of CaCO3 is relatively large, and the stress of CaCO3 particles existing in the PVC matrix is relatively uniform. The incomplete CaCO3 particles at the boundary are prone to stress concentration, however, the incomplete CaCO3 particles at the boundary appear unfrequently, which does not affect the overall mechanical properties of the composite.

The strain results of 10%-CaCO3/PVC composite is shown in Fig. 5. In the simulation mode, the fixed connection method is that the CaCO3 particles and the PVC matrix are constructed as a composite material. Therefore, the overall strain is relatively uniform. The connection positions and fixed constraints of CaCO3 particles and PVC matrix are relatively uniform. Larger strain occurs on the bottom surface.

Fig. 4 Stress results. (a) overall, (b) PVC, (c) internal PVC, (d) CaCO3.

Fig. 5 Strain results. (a) overall, (b) PVC, (c) internal PVC, (d) CaCO3.

The deformation of 10%-CaCO3/PVC composite is shown in Fig. 6. The CaCO3 particles are filled in PVC matrix in a random way, so the distribution of CaCO3 particles in PVC matrix is not uniform. Therefore, the mechanical properties of different parts are not consistent, and the deformation of each part is different under the same tension. However, on the whole, the deformation of each part shows similar tendency. The closer the tensile position is, the greater the deformation is. The deformation of each layer with the same distance from the tensile position is not different, which is in the same order of deformation.

For the condition of CaCO3 ratios with 0%, 5%, 10%, 15%, 20%, 25%, and 30%, the stress results of PVC and CaCO3 under the tensile strength of 40MPa are shown in Fig. 7, and the strain results are
shown in Fig. 8. It can be observed that, the stress and strain of PVC and CaCO₃ fluctuate with the increase of the CaCO₃ ratio. When the CaCO₃ ratio is 10%, the stress and strain of PVC and CaCO₃ both appear peak value. Since the CaCO₃ particles inside the PVC matrix are relatively sparse at this condition, the CaCO₃ cannot form a transfer network, and it is difficult to transfer the force. Therefore, the extrusion between CaCO₃ particles and PVC is intensified, and the stress and strain appear peak value. When the CaCO₃ ratio reaches 25%, the PVC stress and strain show the lowest value, and the stress and strain of CaCO₃ are not too large. Therefore, CaCO₃ ratio of 25% is a better choice. Once the CaCO₃ ratio reaches 30%, the CaCO₃ particles appear obvious aggregation in the PVC matrix, which will intensify the stress concentration effect and cause a significant increase in strain. The elastic modulus of CaCO₃ material is relatively large, therefore, under the same pressure, the deformation shows a downward trend with the increase of CaCO₃ ratio. The overall deformation is approximately inversely proportional to the CaCO₃ ratio, which follows to the basic deformation law of elastic materials. The filling of CaCO₃ in the PVC matrix does not change the basic characteristics of each other's elastic materials, and the new composite materials also have better elastic properties.

Fig. 6 Deformation in tensile direction.  
(a) overall, (b) PVC, (c) internal PVC, (d) CaCO₃.

Fig. 7 Stress curve under tension.  
Fig. 8 Strain curve under tension.

Fig. 9 Deformation curve under tension.

The deformation result in the tensile direction is shown in Fig. 9. As the CaCO₃ ratio increases, the deformation shows a downward trend. When the CaCO₃ ratio is less than 25%, the deformation is...
approximately inversely proportional to the CaCO₃ ratio, which follows to the basic deformation law of elastic materials. When the CaCO₃ ratio reaches 30%, the deformation of PVC suddenly becomes larger. This is because the CaCO₃ particles aggregate in the PVC matrix, and the material in the sparse part of the CaCO₃ particles undergoes greater deformation under the tensile loading.

According to Equ. (1) and simulation result, the tensile properties of CaCO₃/PVC composites with different CaCO₃ ratios is shown in Table 1. According to Table 1, the tensile properties of 25%-CaCO₃/PVC composites show better improvement. For pure PVC, the stiffness of 25%-CaCO₃/PVC composite material increases by 46.23%, the stress of PVC decreases by 23.27%, and the strain of PVC decreases by 22.81%.

| CaCO₃ ratio | Elastic Modulus (MPa) | Increase of stiffness | Reduction of PVC stress | Reduction of PVC strain |
|-------------|-----------------------|-----------------------|-------------------------|------------------------|
| 0           | 6451.6                | /                     | /                       | /                      |
| 5%          | 6666.7                | 3.33%                 | -7.28%                  | -7.22%                 |
| 10%         | 6944.4                | 7.64%                 | -182.39%                | -182.13%               |
| 15%         | 7751.9                | 20.14%                | 7.49%                   | 4.56%                  |
| 20%         | 8032.1                | 24.50%                | 15.19%                  | 15.21%                 |
| 25%         | 9434.0                | 46.23%                | 23.27%                  | 22.81%                 |
| 30%         | 7936.5                | 23.02%                | -132.23%                | -138.4%                |

3.2. Compressive properties
For CaCO₃/PVC composites with CaCO₃ rates of 0, 5%, 10%, 15%, 20%, 25% and 30% under a pressure of 40MPa, the results of stress and strain are shown in Fig. 10 and Fig. 11, respectively. When the CaCO₃ ratio is between 0 and 25%, the stress and strain of CaCO₃ and PVC fluctuate. This is because the CaCO₃ particles are randomly filled into the PVC matrix, and the CaCO₃ particles in the PVC matrix are not uniform. Therefore, the fluctuation of stress and strain within a certain range is normal. When the CaCO₃ ratio reaches 30%, since the CaCO₃ particles appear obvious aggregation in the PVC matrix, the concentration effect of stress and strain is intensified.
The deformation of the CaCO₃/PVC composite in the direction of pressure is shown in Fig. 12. As shown in Fig. 12, the deformation decreases with the increase of CaCO₃ ratio, which follows to the basic deformation law of elastic materials. In addition, the compressive properties of CaCO₃/PVC composites with different CaCO₃ ratios are shown in Table 2. Under compressive loading, the stiffness improvement of 30%-CaCO₃/PVC composite material is the best, which reaches 72.22%. However, 30%-CaCO₃/PVC composite materials are difficult to obtain through ordinary filling process. What’s more, the stress and strain of PVC increase sharply at that condition, which is not helpful for the improvement of mechanical properties. Both the stiffness and the stress, strain should be taken into account for the improvement of tensile properties, therefore, the 25%-CaCO₃/PVC composite is a better choice. For pure PVC, the stiffness of 25%-CaCO₃/PVC composite increases by 57.63%, the stress of PVC decreases by 18.69%, and the strain of PVC decreases by 18.50%.

Table 2 Calculated compressive properties of CaCO₃/PVC composites.

| CaCO₃ ratio | Elastic Modulus (MPa) | Increase of stiffness | Reduction of PVC stress | Reduction of PVC strain |
|-------------|-----------------------|----------------------|------------------------|------------------------|
| 0           | 7168.5                | /                    | /                      | /                      |
| 5%          | 7633.6                | 6.49%                | -1.62%                 | -1.57%                 |
| 10%         | 8510.6                | 18.72%               | -134.44%               | -135.04%               |
| 15%         | 9569.4                | 33.49%               | -54.59%                | -56.69%                |
| 20%         | 9803.9                | 36.76%               | -143.99%               | -144.88%               |
| 25%         | 11299.4               | 57.63%               | 18.69%                 | 18.50%                 |
| 30%         | 12345.7               | 72.22%               | -177.46%               | -177.56%               |

4. Conclusions

The effect of CaCO₃ ratio on the mechanical properties of CaCO₃/PVC composites was studied by numerical simulation in this paper. The conclusions can be summarized as follows:

(1) It can be concluded from the numerical results that, the optimal CaCO₃ ratio of CaCO₃/PVC composite is 25%. The tensile stiffness is increased by 46.23%, and the compressive stiffness is increased by 57.63%.

(2) The stress and strain of CaCO₃/PVC composites under tensile and compressive loading under different CaCO₃ ratios are analysed, in order to avoid cracked CaCO₃/PVC composites of high-rigidity. Under tensile loading, the PVC stress of 25%-CaCO₃/PVC composite is reduced by 23.27%, while the corresponding PVC strain is reduced by 22.81%. Under compressive loading, the PVC stress is reduced by 18.69%, and the PVC strain is reduced by 18.50%.

(3) The numerical method can provide a way for searching the optimal ratio of CaCO₃/PVC composite, reducing the cost of testing, and shortening the development period. At the same time, this method can be applied to the research of other kinds of composite with powder filled.

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