Fabrication and properties of HDPE/CF/CaCO₃/PE-g-MAH quaternary composites

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Abstract. In this research, carbon fiber (CF) was taken as reinforcing filler, nano calcium carbonate (CaCO₃) was taken as toughener, maleic anhydride grafted polyethylene (PE-g-MAH) was taken as compatibilizer for high density polyethylene (HDPE) modification. Through orthogonal test, the influence of different amount of ingredient CF, CaCO₃ and PE-g-MAH on the mechanical properties of the HDPE composites was researched. The optimal composition of the quaternary composites with the good toughness and high strength was obtained.

1. Introduction

High density polyethylene (HDPE) is a kind of non-polar thermoplastic resin which has high crystalline degree. Comparing with engineering plastics product, the application of HDPE product is limited by its low strength, low hardness and low environmental stress crack resistance [1-3]. So that it cannot be widely used as structural material. CF is a kind of reinforcing material which has excellent properties [4, 5]. The adding of CF can obviously improve the tensile strength, bending strength and stiffness of HDPE, meanwhile the impact strength which displays the toughness of the material can have a sharp decrease. PE-g-MAH can improve the interfacial compatibility of CF and HDPE and thus improve the impact strength of the material. As an excellent toughener, nanometer scale inorganic rigid filler CaCO₃ can largely increase the toughness of material [6].

In this research, firstly, CaCO₃ was added into HDPE/CF blend system, the impact of CaCO₃ on mechanical properties of blend system was studied. Secondly, CF as reinforcing filler, CaCO₃ as toughener, and PE-g-MAH as compatibilizer were considered as three main factors which influence the mechanical properties of HDPE matrix material. In order to investigate the effect of the relative amount of the three components on the mechanical properties of blend system and thus get a HDPE composite with high strength and high toughness, an orthogonal test was designed.

2. Experimental

2.1. Materials

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High density polyethylene (60550AG-Ⅱ) supplied by PetroChina Lanzhou Petrochemical Company; Carbon Fiber (filament diameter 0.7 μm, length 5 mm) supplied by China Carbon Composite Materials Co., LTD; PE-g-MAH (2909, with a grafting ratio of 1.2%) supplied by Shenzhen HuaLin Chemical Co., LTD; Nanoscale CaCO₃ (average grain diameter 60-80 nm, activating rate larger than 90%) supplied by Shanghai Hongqing New Materials Co., LTD.

2.2. Experimental design
HDPE (100 phr/per hundred resin), CF (15 phr), CaCO₃ (varies from 0 to 15 phr, each 5 phr as a step) were mixed and four different blends were prepared, marked as CaCO₃0, CaCO₃5, CaCO₃10 and CaCO₃15, respectively.

### Table 1. Factor levels designed in orthogonal experiment.

| Level | Factor       |
|-------|--------------|
|       | A (CF/phr)   | B (CaCO₃/phr) | C (PE-g-MAH/phr) |
| 1     | 5            | 5             | 2               |
| 2     | 10           | 10            | 4               |
| 3     | 15           | 15            | 6               |

The orthogonal test was designed as follows: amount of CF (A), CaCO₃ (B) and PE-g-MAH (C) and they were taken as the factors which affected the mechanical properties of blend system. Each factor has three levels thus the orthogonal experiment L₉(3⁴) was applied. The factors and level settings were shown in table 1. The scheme of orthogonal experimental design was shown in table 2. The optimum recipe can be found after nine groups of test.

### Table 2. The orthogonal experiment design.

| Test number | Factor | Sample number |
|-------------|--------|---------------|
|             | A/phr  | B/phr | C/phr | AᵢBᵢCᵢ |
| 1           | 5      | 5     | 2     | A₁B₁C₁ |
| 2           | 5      | 10    | 4     | A₂B₂C₂ |
| 3           | 5      | 15    | 6     | A₁B₁C₃ |
| 4           | 10     | 5     | 4     | A₂B₂C₂ |
| 5           | 10     | 10    | 6     | A₂B₂C₃ |
| 6           | 10     | 15    | 2     | A₂B₂C₁ |
| 7           | 15     | 5     | 6     | A₃B₃C₃ |
| 8           | 15     | 10    | 2     | A₃B₃C₁ |
| 9           | 15     | 15    | 4     | A₃B₃C₂ |

2.3. Composites fabrication procedure
Take ethyl alcohol as solvent to prepare 1 wt.% KH560 silane coupling agent solution. CaCO₃ was mixed with the solution in an environment away from light and soaked for an hour. Then the sample was filtered and washed by deionized water for three to four times, dried under 70°C and cooled for further use. According to the recipe in table 2, blend the dried materials on double-roller blending rolls. The order of adding materials should be: adding CF into blend system after milling HDPE on an open mill for 10mins. After the blend was well mixed, CaCO₃ was added into the system. Finally the compatilizer PE-g-MAH was added into the blend system.

2.4. Characterizations
An electronic universal testing machine was used for tensile strength test. The specimens of HDPE matrix composites for tensile test were prepared by injection molding. The method and standard of the test shall refer to China GB/T 1040.2-2006 Standard.

Izod impact tests were conducted by Izod impact test machine (XJU-5.5 type, Chengde Jinjian) under room temperature. The specimens of HDPE matrix composites for impact test were prepared by injection molding. Each value obtained represented the average of five samples.

An electronic universal testing machine was used for bending strength test. When running the test, all the stress was loaded at the same direction. The distance between the two fulcrums was 64 mm.

The liquid-nitrogen-frozen fractured HDPE matrix composites with different contents of CF, CaCO₃ and PE-g-MAH were studied using a JSM-6460LV SEM (JEOL). The SEM samples were etched by acetone for a given time and gold-sputtered prior to observation.

3. Results and discussion

3.1. The mechanical properties of HDPE/CF/CaCO₃ system

The effect of nano calcium carbonate loading on tensile strength and bending strength of CF (15 phr) strengthened HDPE was shown in figures 1 and 2. As shown, the adding of nano calcium carbonate lowered the stiffness of material. When the CaCO₃ was added to 15 phr, tensile strength and bending strength of material reached the minimum value at the same time (35.95 MPa and 40.11 MPa respectively). When compared with HDPE/CF binary system, the tensile strength and bending strength decreased to 82.64% and 91.45%, respectively. This suggests that when the amount of nano CaCO₃ is high, the combination between the different phases in the system is not so good which resulted in deterioration of materials’ ability to resist deformation.

![Figure 1](image1.png)

**Figure 1.** Effect of nano CaCO₃ on the tensile strength of the HDPE composites.

![Figure 2](image2.png)

**Figure 2.** Effect of nano CaCO₃ on the bending strength of the HDPE composites.
When the amount of CaCO$_3$ is 10 phr, the tensile strength of HDPE/CF/CaCO$_3$ system (40.07 MPa) has decreased slightly comparing to HDPE/CF binary system (43.5 MPa), but it showed a 58.00% improvement when compared with HDPE (25.36 MPa); the bending strength reached 45.32 MPa, showed a slight increase comparing to HDPE/CF binary system.

The effect of nano CaCO$_3$ on the impact strength of the blend system was shown in figure 3. When the amount of CaCO$_3$ was 5 phr, the impact strength of system was 7.19 kJ/m$^2$, showing a slight decrease comparing with that of HDPE/CF binary system (7.4 kJ/m$^2$). With the increasing of CaCO$_3$ amount, the impact strength of system reached 8.61 kJ/m$^2$ when amount of CaCO$_3$ was 10 phr, showed a 16.35% increase comparing with that of HDPE/CF binary system. When the amount of CaCO$_3$ was 15 phr, the impact strength dropped to 8.13 kJ/m$^2$. As analyzed, when the amount of CaCO$_3$ was 10phr, polar CF and non-polar CaCO$_3$ could both be well contacted with matrix resin, the density of disperse increased. Among the system, CaCO$_3$ can be seen as a third phase which can transmit stress, CF played the role of reinforcing agent. In consequence, the impact strength of the composites was obviously improved. But the amount of CaCO$_3$ shall not be too much. Excessive CaCO$_3$ can make the interfacial properties between each component to be worse. CaCO$_3$, as a relatively plentiful phase, were likely to make direct contact with CF. As a result, stress cracking were more likely to occur when the material was under external impact.

3.2. Orthogonal test and range analysis

The orthogonal test was carried out according to table 2. The results are shown in table 3. The impact strength values in table 3 were range analyzed.

**Table 3. Results of orthogonal test.**

| Test number | Impact strength kJ/m$^2$ |
|-------------|-------------------------|
| A$_1$B$_1$C$_1$ | 6.806                   |
| A$_1$B$_2$C$_2$ | 7.698                   |
| A$_1$B$_3$C$_3$ | 6.612                   |
| A$_2$B$_1$C$_2$ | 4.266                   |
| A$_2$B$_2$C$_3$ | 6.422                   |
| A$_2$B$_3$C$_1$ | 6.314                   |
| A$_3$B$_1$C$_2$ | 8.851                   |
| A$_3$B$_2$C$_1$ | 6.106                   |
| A$_3$B$_3$C$_2$ | 5.872                   |

The impact strength of quaternary blending system showed a decreasing trend when the adding
amount of CF was low. The reason is speculated as follows: since the quantity of CF in each unit section was low, the average stress that CF in each unit section borne was high. Stress concentrated in the position of CF. As results, either CF was pulled out easily, or crack occurs in the interface between CF and matrix resin, both leaded to the sharp decrease of impact strength. When CF is further added to 15 phr, impact strength of quaternary blending system showed an increasing trend, the mechanism of such phenomenon is speculated as follows: since the quantity of CF in each unit section increased, along with the existence of compatilizer PE-g-MAH which improved the interfacial compatibility of CF with HDPE, CF could deliver more impact energy. When the material is impacted, the possibility of interfacial debonding dropped. Thus, the impact strength of material is improved.

With the increase of CaCO₃ amount, the impact strength of blending system rose at the beginning and then dropped down, similar to the trend in ternary system. The impact strength reached the peak when CaCO₃ amount is 10 phr. CaCO₃ can demonstrate the strengthen ability when its amount is low. However, CaCO₃, as polar filler, have low compatibility with non-polar matrix. Agglomeration occurs among CaCO₃ particles, the interfacial compatibility also became worse. These are the main reasons led to the sharp decrease of impact strength.

| Table 4. Results of range analysis of impact strength in orthogonal test. |
| --- | --- | --- | --- |
| Mean impact strength of every level, kJ/m² | Factors A/phr | B/phr | C/phr |
| k1 | 6.875 | 6.641 | 6.407 |
| k2 | 5.667 | 6.742 | 5.945 |
| k3 | 6.943 | 6.266 | 7.295 |
| Range | 1.086 | 0.476 | 1.350 |

When the amount of PE-g-MAH was 6 phr, the impact strength of quaternary system reached the maximum. When the amount of PE-g-MAH was low, it could not be well mixed with CaCO₃ and CF fillers, the interaction between four kinds of component was weak; the phase interfaces was obvious so the material is easy to break at the interfaces when impacted by external force. Thus the material showed low impact strength. When the addition of PE-g-MAH increased from 4 phr to 6 phr, the average impact strength of blend system climbed from 5.945 kJ/m² to 7.295 kJ/m². The increase rate reached 22.71%. The reason may be that the increase of compatilizer had strengthened the interaction between CF, CaCO₃ and matrix. That is, the ethylene chain segments grafted polyethylene affined well with the HDPE chain, at the same time, the grafted MAH group was strong chemistry bounded to the surface of CF and CaCO₃. PE-g-MAH showed the function of “bridge” among fillers and matrix and improved the surface condition among each component. So the impact strength of filled system had improved.

3.3. The determine of the optimum recipe
According to the results of range analysis in table 4, the maximum value of range of factor C (the amount of PE-g-MAH) is 1.350. The range reflects the degree of effect that the factor made to index. The results showed that among the quaternary system, the amount of PE-g-MAH has the greatest influence to the mechanical properties of blend system, i.e. the amount of PE-g-MAH is the main factor. From figure 3 we can conclude, the level of C (the amount of PE-g-MAH) should be C3.

Then, the range of factor A (the amount of CF) is 1.086. The results showed that the amount of PE-g-MAH has great influence to the mechanical properties of blend system. From table 4 we can conclude, the level of A (the amount of CF) should be A3. Then, the range of factor B (the amount of CaCO₃) is 0.476. The results showed that the amount of CaCO₃ has little influence to the mechanical properties of blend system. Thus the factor C is the secondary factor. Also we can conclude, the level of B (the amount of CaCO₃) should be B2.

From the above, the conclusion can be gotten the optimum recipe should be A₃B₂C₃. That is, when the amount of matrix resin HDPE was 100 phr, the amount of CF was 15 phr, the amount of CaCO₃
was 10 phr and the amount of PE-g-MAH was 6 phr, the impact strength of blend system may reach the maximum.

Recipe A3B2C3 did not occur in the scheme of orthogonal test. So we did a further test with the blending system of the recipe A3B2C3. The properties of recipe A3B2C3 and pure HDPE were compared as table 5. The impact strength indicates the toughness of material had risen 18.74%, from 8.75 kJ/m$^2$ (pure HDPE) to 10.39 kJ/m$^2$ (A3B2C3). This had experimentally verified the accuracy of influence each factor level made on the impact strength of material. Meanwhile, tensile strength and bending strength were also great. Tensile strength of recipe A3B2C3 rose from 25.36 MPa (pure HDPE) to 42.17 MPa, which was a 66.29% increase. Bending strength of recipe A3B2C3 rose from 21.48 MPa (pure HDPE) to 60.12 MPa, which was a 137.52% increase.

|                         | Pure HDPE | HDPE/CF (15 phr) | A3B2C3 |
|-------------------------|-----------|------------------|--------|
| Impact strength (KJ/m$^2$) | 8.75      | 7.41             | 10.39  |
| Tensile strength (MPa)  | 25.36     | 43.51            | 42.17  |
| Bending strength (MPa)  | 21.48     | 43.86            | 60.12  |
| Vicat softening temperature (˚C) | 70.5 | 80.5              | 80.6   |
| MFR (g/10 min, 2.16 Kg) | 6.3       | 2.6              | 5.7    |

From the above results, we can conclude that recipe A3B2C3 is the composite material which has obvious strengthening effect and best toughness obtained by the experiment. The reason maybe the compatibilizer PE-g-MAH improved the dispersion of nano CaCO$_3$ and CF. Furthermore, it enhanced the interface bonding between the fillers and HDPE matrix.

The heat resistance of A3B2C3, HDPE and HDPE/CF were also compared in table 5. As shown, the vicat softening temperature of A3B2C3 reached 80.6˚C, showed 14.33% increase when compared with HDPE (70.5˚C), showed a slightly increase when compared with HDPE/CF binary system. It was clear that A3B2C3 has good heat resistance.

The melt flow rate (MFR) of A3B2C3, HDPE and HDPE/CF were investigated. As shown, the MFR value of A3B2C3 reached 5.7 g/10 min, showed slightly decrease when compared with HDPE (6.3 g/10 min). Meanwhile it showed a 142.69% increase when compared with HDPE/CF binary system (2.6 g/10 min) in which the amount of CF is 15 phr. It was clear that A3B2C3 has better processing fluidity than the HDPE/CF binary system.

**Figure 4.** SEM micrographs of HDPE/CF/CaCO$_3$ ternary composites (a); HDPE/CF/ CaCO$_3$/PE-g-MAH quaternary composites (b).

From figures 4(a) and 4(b), we can see that CF and CaCO$_3$ have better dispersion in the HDPE/PE-g-MAH composite matrix than the pure HDPE matrix. Some hollow holes were discovered...
on the impact fractured surface. Materials broke at the same layer that meant there was no stress concentration inside material, at the break position it was uniformly forced and there were no large crack occurs at the break. As shown, CF and matrix resin were well wrapped, CaCO$_3$ were also well deposited in matrix resin. PE-g-MAH improved the interfacial adhesion between the fillers and the HDPE matrix. From above we can conclude that there were fine combinations among matrix resin and fillers.

4. Conclusions

In this study, the HDPE/CF/CaCO$_3$/PE-g-MAH quaternary composites were fabricated and their properties were characterized. CF as reinforcing filler, CaCO$_3$ as toughener, and PE-g-MAH as compatibilizer were considered as three main factors which influence the mechanical properties of HDPE matrix material. Orthogonal test and range analysis were designed and conducted. The optimum recipe obtained from the experiment was A$_3$B$_2$C$_3$, i.e. the amount of matrix resin HDPE was 100 phr, the amount of CF was 15 phr, the amount of CaCO$_3$ was 10 phr, and the amount of PE-g-MAH was 6 phr. Analyses were taken with the result of orthogonal test. The impact strength had risen 38.53%, from 7.5 kJ/m$^2$ (pure HDPE) to 10.39 kJ/m$^2$ (A$_3$B$_2$C$_3$). It had experimentally verified the accuracy of influence each factor level made on the impact strength of material. Meanwhile, tensile strength and bending strength were also great. The vicat softening temperature which indicates the HDPE/CF/CaCO$_3$/PE-g-MAH quaternary composites have good heat resistance and processing fluidity. From the micro morphology measurement conducted by SEM, it was concluded that all fillers in the composites were well dispersed and interface bonding was good.

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