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Mechanical enhancement of ripples and dimples in CaCO₃/low-density unsaturated polyester resin composites

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Abstract

Incorporation of different fine grain calcium carbonate into CaCO₃/l-low-density unsaturated polyester resin (LDUPR) composites was studied and evident mechanical enhancement of CaCO₃ on composites was investigated. Preliminary experiment results indicated that proper content of CaCO₃ was less than 30.00 phr (parts per hundreds of resin), suitable preparation temperature range was from 72.0 °C to 80.0 °C, and initiator content was 1.80 phr. Optimal preparation conditions of CaCO₃/LDUPR samples were obtained with the presence of 25.00 phr CaCO₃ and 2.50 phr NH₄HCO₃ at 76.0 °C based on preliminary experiments. The lowest apparent density of A-CaCO₃/LDUPR composite was 0.53 ± 0.02 g · cm⁻³ with a compressive strength of 20.27 ± 0.51 MPa · g⁻¹ · cm³, and the highest specific compressive strength of the sample was 38.25 ± 1.43 MPa · g⁻¹ · cm³. It is attributed to the hindrance to cross-linking between unsaturated polyester and styrene, and to the decrease of exothermic heat of the polymerization, which was caused by the existence of CaCO₃. Unusual matrix microstructure with regular ripples and dimples formed by CaCO₃, and the particular mechanical enhancement of regular ripples and dimples in composites were explored. ‘CaCO₃ reefs’ concept, reefs-induced ripples, dimples of streams flowing, and resolution of external force with major force further being consumed models comprised the regulated mechanical enhancement of CaCO₃ in CaCO₃/LDUPR composites. This particular polymerization retarding and mechanical strengthening were obvious for the finest grain CaCO₃.

1. Introduction

With increasing demand of economic efficiency and environmental protection, low cost and high specific strength product has received attention lately as for unsaturated polyester resin. In the case of the tendency, low-density unsaturated polyester resin (LDUPR) and its composite materials, which present less resin cost, low apparent density and high specific compressive strength, have been the growing highlight of studies for UPR composite materials [1–3].

The preparation of LDUPR and its composite materials have progressed over the past decade. Guo et al [4], Zhang et al [5] and Ji et al [1] presented new organic foaming methods or novel mechanisms of LDUPR preparation. Xu et al prepared LDUPR utilizing the cooperation of sodium bicarbonate and azodiisobutyronitrile [2]. At high temperature, Zhu et al explored the LDUPR preparation with the presence of sodium carbonate/hydrazide/ammonium mixture [6]. Novel mild-thermal fabrication of chopped glass fiber/LDUPR composite via NH₄HCO₃ was presented by Guo et al [3].

Besides researches of LDUPR and fiber reinforced LDUPR, it is essential to incorporate fillers, such as calcium carbonate, silica, talc, alumina hydrates into resin to reduce the cost of composites and to improve the mechanical properties of composites [7, 8]. Calcium carbonate is the most commercial inorganic filler exhibiting high volume, low cost, good stability, nontoxic, and non-black specialties [9–11]. Gupta et al [12] investigated the effect of CaCO₃ filler on fiber-reinforced polymer composites (FRP), and proposed a hybrid filler composition to optimize mechanical characteristics. He et al [13] pointed out that the toughening of vinyl
ester resin composite, which was with the presence of calcium carbonate in different particle sizes, was 27%–45% higher than that of pure resin. The dominant feature of CaCO₃ in LDUPR and LDUPR composites is crucial for the versatility, the economics efficiency, and the mechanical properties of composites. Moreover, the addition of CaCO₃ might provide CaCO₃/LDUPR composites with competitive performances in case of using LDUPR alone. However, the effects of CaCO₃ on CaCO₃/LDUPR composites preparation, on the curing of UPR during the process, and on the microstructural specialties reported so far are incomplete or shallow.

In this study, three kinds of fine grain CaCO₃ in different particle sizes were used to prepare CaCO₃/LDUPR composites. The effects of fine grain CaCO₃ on the preparation of CaCO₃/LDUPR, on the cross-linking between unsaturated polyester and styrene, on the microstructure evolution of CaCO₃/LDUPR, and on the improvement of CaCO₃/LDUPR mechanical properties were investigated and innovated strengthening mechanism was presented.

2. Experimental

2.1. Materials

UPR (Type P17-902) was the orthophthalic polyester resin of Jinling Aliancys Resins Co., Ltd., China, with an unsaturated polyester content of 63–66 wt%, viscosity of 1300–1500 mPa·s (23 ± 1 °C), and an acid value from 15 mg KOH · g⁻¹ to 19 mg KOH · g⁻¹. At ambient temperature, unsaturated polyester resin was a glue without mechanical properties. As for the cured resin, the apparent density of was 1.12 ± 0.01 g · cm⁻³, the compressive strength was 28.19 ± 0.32 MPa, and the specific compressive strength was 25.17 ± 0.91 MPa · g⁻¹ · cm⁻³.

CaCO₃ (Type carb-5) was purchased from Nanjing Omya fine chemical Co., Ltd. China with a purity ≥98%, and treated with coupling agent KH570 to enhance the binding performance of filler and UPR glue to prevent agglomeration. Three kinds of fine grain CaCO₃, such as A-CaCO₃ (d₅₀ = 2.7 × 10⁻⁶ m, d₉⁷ = 1.0 × 10⁻⁵ m), B–CaCO₃ (d₅₀ = 3.0 × 10⁻⁶ m, d₉⁷ = 1.5 × 10⁻⁵ m), and C–CaCO₃ (d₅₀ = 3.20 × 10⁻⁶ m, d₉⁷ = 1.8 × 10⁻⁵ m), were applied in the study.

NH₄HCO₃, as a foaming agent, was produced by Shanghai No. 4 Reagent & H.V. Chem. Co., Ltd., China, and its content was 99 wt%.

Tert-butylperoxy benzene (TBPB, 98 wt%) was the initiator for UPR polymerization, which was produced from Akzo Nobel N.V., Netherlands.

PMR-EZ, as an external release agent, was produced from CHEM-TREND Co., Ltd., USA.

Dioctyl phthalate (DOP) was the solvent applied in volumetric gas-burette experiments obtained from Shanghai Ling Feng chemical reagents Co., Ltd., China, and its content ≥99 wt%.

2.2. Characterization

2.2.1. Viscosity testing

Referring to the ISO 3219.1993 standard ("Unsaturated polyester resin viscosity measurement") the viscosity of resin glue was measured by use of digital rotatory viscometer NDJ-79A, which was made by Shanghai Changji Geological Instrument Co., Ltd. China. The sensor accuracy was 2% F.S. and the relative humidity was ≤80%.

2.2.2. Decomposition of NH₄HCO₃ measurement

The decomposition of NH₄HCO₃ was detected through a volumetric gas-burette experiment [14, 15]. Decomposition temperature-bleed volume curve of NH₄HCO₃ was heated from ambient temperature (20.0 °C) to 100.0 °C at the heating rate of 2 °C · min⁻¹, and bleed volume curves of NH₄HCO₃ decomposition at a certain temperature were also analyzed.

2.2.3. Gel time determination

GT-2a gel time meter (Lian’an Fengyuan Electronics Co., Ltd., China, with a temperature accuracy of ±0.1 °C, and working temperature ≤ 230 °C) was applied to detect the gel time of UPR glue according to the standard ISO 2554:1997 ("Test Methods of Unsaturated Polyester Resins").

2.2.4. Properties detection of CaCO₃/LDUPR composites

Apparent density (ρ) of sample was tested according to standard ISO 845–2006. Compressive strength (P) of sample was measured according to standard ISO 844:2014 at an ambient temperature of 23 ± 2 °C, and relative humidity was 50 ± 5% utilizing electronic universal testing machine (WDW3100, produced by Changchun Xinke Instrument Co. Ltd., China, the accuracy was 0.5%, and the maximum pressure was 100 kN). A parallel experiment including five replicated samples was processed for each formulation.
2.2.5. Thermal analysis
Non-isothermal differential scanning calorimetry (DSC) of samples was examined by using NETZSCH DSC 204 (NETZSCH Scientific Instruments Trading Ltd., Germany), where the nitrogen atmosphere of samples sealed in an aluminum crucible was kept at 30 ml · min⁻¹, the temperature accuracy of the instrument was ±0.1 °C, the heating rate of the experiment was 10 °C · min⁻¹, and the mass of the sample was 5–10 mg.

2.2.6. Scanning electron morphology
Fracture surfaces of samples were observed by SEM (JEOL JSM-6510, Japan) at an accelerating voltage of 15 kV in high-vacuum mode. Surface sections of samples were sputtered with gold to enhance the electronic conductivity.

3. Results and discussion

3.1. Effect of CaCO₃ on the viscosity of resin glue and on the decomposition of NH₄HCO₃
CaCO₃ affected the viscosity of resin glue. The maximum content of CaCO₃ was suggested to be controlled within 65.00 phr for UPR [16]. In this study, the content of CaCO₃ was controlled no more than 35.00 phr, considering the motion and the distribution of bubbles (which were caused by decomposition of NH₄HCO₃) in resin glue. Viscosity changes of UPR glue, which contained variant contents and different particle size CaCO₃, were illustrated in figure 1.

Figure 1 shows that, with the presence of CaCO₃ ≥30.00 phr, the viscosity of UPR glue is higher than 4000 mPa.s accompanied with difficult distribution of CaCO₃ in resin glue.

Based on the above viscosity experiment, 10.00 phr, 20.00 phr, and 30.00 phr CaCO₃ was applied separately to examine the effect of particle size of CaCO₃ on the thermal decomposition of NH₄HCO₃ (see figure 2). Figure 2(a) indicates that the temperature range of the maximum thermal decomposition rate of the NH₄HCO₃ was from 70 °C to 86 °C, for three different particle sizes of CaCO₃. The gel time of resin glue in the preparation of CaCO₃/LDUPR should be controlled in the range of 25.0 min to 35.0 min [17–19], where, the gel time of resin glue lasted 4.0 min [20, 21]. Figure 2(b) shows that the bleed time of NH₄HCO₃ was 39.3–28.9 min in the temperature range of 72.0–80.0 °C. Therefore, the most suitable preparation temperature range of CaCO₃/LDUPR sample was set from 72.0 °C to 80.0 °C.

Considering the dosage of initiator should be controlled no more than 3.00 phr [1, 18] in practice, the adding amount of initiator was tried to set as 1.50 phr, 2.00 phr, and 2.50 phr to detect the change of gel time. Under the condition, the gel time of resin glue at 72.0 °C, 76.0 °C, and 80.0 °C was detected separately, where, both CaCO₃ (with the presence of 10.00 phr, 20.00 phr, and 30.00 phr separately) and NH₄HCO₃ (with the presence of 1.00 phr, 2.00 phr, 3.00 phr separately) existed in resin glue. These gel time experiment results are shown in table 1.

Table 1 illustrates that proper adding amount of initiator should be between 1.50 phr and 2.00 phr. After that, 1.80 phr initiator was set as the optimal content of initiator, and gel time experiment was repeated. It is concluded that the most suitable gel time was 25.3–34.2 min corresponding to 1.80 phr initiator.
Figure 2. Curves of (a) decomposition temperature-bleed volume of NH$_4$HCO$_3$ with CaCO$_3$, and (b) decomposition temperature-bleed volume of NH$_4$HCO$_3$ in the temperature range from 70.0 °C to 86.0 °C.

Table 1. Gel Times of resin glue with different content of initiator.

| Temperature (°C) | CaCO$_3$ content (phr) | Initiator content (phr) | NH$_4$HCO$_3$ content (phr) | Gel time (min) |
|----------------|------------------------|------------------------|----------------------------|----------------|
| 72.0 | 10.00 | 1.00 | 35.6 | 34.2 | 33.8 | 34.1 | 28.7 | 29.1 | 29.3 |
| | | 2.00 | 36.1 | 34.4 | 34.6 | 34.9 | 29.7 | 29.6 | 29.6 |
| | | 3.00 | 36.9 | 34.1 | 34.5 | 34.9 | 29.6 | 28.6 | 28.8 |
| 76.0 | 10.00 | 1.00 | 36.5 | 36.0 | 36.2 | 34.2 | 33.8 | 34.1 | 28.7 | 29.1 | 29.3 |
| | | 2.00 | 36.1 | 34.4 | 34.6 | 34.9 | 29.7 | 29.6 | 29.6 |
| | | 3.00 | 36.9 | 34.1 | 34.5 | 34.9 | 29.6 | 28.6 | 28.8 |
| 80.0 | 10.00 | 1.00 | 37.0 | 37.4 | 37.0 | 36.2 | 36.2 | 34.2 | 33.8 | 34.1 | 28.7 | 29.1 | 29.3 |
| | | 2.00 | 36.1 | 34.4 | 34.6 | 34.9 | 29.7 | 29.6 | 29.6 |
| | | 3.00 | 36.9 | 34.1 | 34.5 | 34.9 | 29.6 | 28.6 | 28.8 |
Table 2. Orthogonal experiment design and results of A-CaCO₃/LDUPR.

| Experimental serial number | Preparation temperature (°C) | NH₄HCO₃ content (phr) | CaCO₃ content (phr) | ρ (g · cm⁻³) | P (MPa) | Pᵥ (MPa · g⁻¹ · cm³) |
|----------------------------|----------------------------|-----------------------|---------------------|-------------|---------|-----------------------|
| 1                          | 72.0                       | 1.00                  | 10.00               | 0.71 ± 0.02 | 20.64 ± 0.34 | 29.07 ± 1.02 |
| 2                          | 72.0                       | 1.50                  | 15.00               | 0.69 ± 0.01 | 19.62 ± 0.56 | 28.43 ± 0.98 |
| 3                          | 72.0                       | 2.00                  | 20.00               | 0.68 ± 0.02 | 20.52 ± 0.71 | 30.18 ± 1.23 |
| 4                          | 72.0                       | 2.50                  | 25.00               | 0.66 ± 0.04 | 19.48 ± 0.20 | 29.52 ± 1.12 |
| 5                          | 72.0                       | 3.00                  | 30.00               | 0.84 ± 0.02 | 19.32 ± 0.66 | 23.00 ± 0.88 |
| 6                          | 74.0                       | 1.00                  | 15.00               | 0.71 ± 0.01 | 18.88 ± 0.57 | 26.59 ± 1.03 |
| 7                          | 74.0                       | 1.50                  | 20.00               | 0.62 ± 0.03 | 21.16 ± 0.35 | 34.13 ± 1.14 |
| 8                          | 74.0                       | 2.00                  | 25.00               | 0.70 ± 0.04 | 21.96 ± 0.44 | 31.37 ± 1.08 |
| 9                          | 74.0                       | 2.50                  | 30.00               | 0.86 ± 0.01 | 18.84 ± 0.73 | 21.91 ± 1.22 |
| 10                         | 74.0                       | 3.00                  | 10.00               | 0.56 ± 0.03 | 15.80 ± 0.56 | 28.21 ± 0.97 |
| 11                         | 76.0                       | 1.00                  | 20.00               | 0.71 ± 0.02 | 21.37 ± 0.34 | 30.10 ± 1.33 |
| 12                         | 76.0                       | 1.50                  | 25.00               | 0.73 ± 0.01 | 20.46 ± 0.58 | 28.03 ± 1.16 |
| 13                         | 76.0                       | 2.00                  | 30.00               | 0.78 ± 0.04 | 18.81 ± 0.61 | 24.12 ± 1.04 |
| 14                         | 76.0                       | 2.50                  | 10.00               | 0.49 ± 0.03 | 16.51 ± 0.41 | 33.69 ± 0.84 |
| 15                         | 76.0                       | 3.00                  | 15.00               | 0.44 ± 0.02 | 17.18 ± 0.39 | 39.05 ± 1.26 |
| 16                         | 78.0                       | 1.00                  | 25.00               | 0.75 ± 0.04 | 22.51 ± 0.47 | 30.01 ± 1.31 |
| 17                         | 78.0                       | 1.50                  | 30.00               | 0.86 ± 0.01 | 23.04 ± 0.28 | 26.79 ± 1.14 |
| 18                         | 78.0                       | 2.00                  | 10.00               | 0.55 ± 0.03 | 17.36 ± 0.36 | 31.56 ± 0.97 |
| 19                         | 78.0                       | 2.50                  | 15.00               | 0.63 ± 0.04 | 20.18 ± 0.59 | 32.03 ± 1.24 |
| 20                         | 78.0                       | 3.00                  | 20.00               | 0.76 ± 0.02 | 18.44 ± 0.66 | 24.26 ± 1.19 |
| 21                         | 80.0                       | 1.00                  | 30.00               | 0.98 ± 0.02 | 22.26 ± 0.70 | 22.71 ± 1.30 |
| 22                         | 80.0                       | 1.50                  | 10.00               | 0.59 ± 0.03 | 17.44 ± 0.65 | 29.56 ± 1.17 |
| 23                         | 80.0                       | 2.00                  | 15.00               | 0.65 ± 0.01 | 19.85 ± 0.59 | 31.51 ± 0.89 |
| 24                         | 80.0                       | 2.50                  | 20.00               | 0.64 ± 0.04 | 20.02 ± 0.63 | 31.28 ± 1.44 |
| 25                         | 80.0                       | 3.00                  | 25.00               | 0.82 ± 0.02 | 24.06 ± 0.42 | 29.34 ± 1.35 |

3.2. Foaming composites of CaCO₃/LDUPR

According to the standard of ISO 3672-2:2001, CaCO₃/LDUPR samples were prepared with a formulation of 100 resin: XNH₄HCO₃: Y CaCO₃: 1.80 TPBB at a certain temperature. The content of NH₄HCO₃ foaming agent (X) should be controlled no more than 3 phr [3, 22]. Values of Y and T were determined in terms of preliminary experiments above, where Y value was no more than 30.00 phr and T was in range from 72.0 °C to 80.0 °C. Under the condition, CaCO₃/LDUPR samples were prepared through orthogonal experiment. Orthogonal experiment is a kind of multifactor and multilevel test design method, which can substantially reduce the number of tests under the condition of ensuring the representativeness of the test [23, 24]. In this study, an orthogonal experiment of L₂⁵(5⁵) (where L is the code name, 25 is the number of test, 5 is the number of different factors, and 5 is the level number for one factor [3, 5]) was designed for the preparation of CaCO₃/LDUPR. X, Y, and T were three different factors. Level numbers for X were varying from 1.00 phr to 3.00 phr with an interval of 0.50 phr. Level numbers for Y were from 10.00 phr to 30.00 phr with an interval of 5.00 phr. Level numbers for T were set from 72.0 °C to 80.0 °C with an interval of 2.0 °C. CaCO₃/LDUPR samples were cured at a preparation temperature for 2 h, and then were cooled down to room temperature and got by demolding. In the orthogonal experiment, a parallel experiment including five replicated samples was processed for each formulation. The orthogonal experiment results are listed in table 2.

Effects of three experimental factors on the ρ and the P of CaCO₃/LDUPR samples were analyzed, and results are summarized in table 3. In table 3, Kᵣ is the average of ρ and Kᵣ is the average of P, which were calculated separately from five values at a level of one single factor. Rᵣ is the range of Kᵣ between Kᵣ max and Kᵣ min, and Rᵣ represents the range of Kᵣ between Kᵣ max and Kᵣ min. As shown in table 3, the Rᵣ value of ρ is 0.10 g · cm⁻³ for the preparation temperature of CaCO₃/LDUPR at 76.0 °C. Effects of the content of A-CaCO₃ and that of NH₄HCO₃ on ρ, P, and on Pᵥ of A-CaCO₃/LDUPR samples at 76.0 °C are illustrated in figure 3.

It is deduced from figure 3 that the optimal conditions for A-CaCO₃/LDUPR preparation is 25.00 phr A-CaCO₃, 2.50 phr NH₄HCO₃ at 76.0 °C, corresponding to ρ min = 0.53 ± 0.02 g · cm⁻³, P = 20.27 ± 0.51 MPa, and Pᵥ max = 38.25 ± 1.43 MPa · g⁻¹ · cm³. As processed above, B-CaCO₃/LDUPR sample exhibits ρ min of 0.59 ± 0.03 g · cm⁻³, P of 21.33 ± 0.48 MPa, and Pᵥ max of 36.15 ± 1.27 MPa · g⁻¹ · cm³. Furthermore, C-CaCO₃/LDUPR sample presents ρ min of 0.64 ± 0.04 g · cm⁻³, P of 21.78 ± 0.39 MPa, and Pᵥ max of 34.03 ± 1.26 MPa · g⁻¹ · cm³. It is illustrated that as the particle size of CaCO₃ increases, the apparent density (ρ) of CaCO₃/LDUPR sample increases, while the specific compressive strength (Pᵥ) decreases. Finer grain CaCO₃, more evident foaming and mechanical enhancement of CaCO₃/LDUPR sample. On the other hand, LDUPR sample, which was obtained with the
presence of 2.50 phr NH$_4$HCO$_3$ at 76.0°C, exhibited $\rho$ of 0.49 ± 0.04 g · cm$^{-3}$, $P$ of 14.87 ± 0.32 MPa, and $P_{\text{comp}}$ of 34.03 ± 1.26 MPa · g$^{-1}$ · cm$^{-3}$.

As for the chopped glass fiber reinforced low-density unsaturated polyester resin (CGR-LDUPR), the apparent density was 0.63 ± 0.02 g · cm$^{-3}$, the compressive strength was 24.29 ± 0.73 MPa, and the specific compressive strength was 38.56 ± 1.02 MPa · g$^{-1}$ · cm$^{-3}$ [3]. It is obviously that the mechanical enhancement of the fine particle CaCO$_3$ was the same as that of CGR-LDUPR. Therefore, the intrinsic relationship between fine grain CaCO$_3$ and polymerization as well as mechanical strengthening is essential to explore.

### 3.3. Mechanical enhancement mechanism

#### 3.3.1. Retardation of CaCO$_3$ to the cross-linking of LDUPR

The effects of three kinds of CaCO$_3$ on the curing process of UPR were characterized by non-isothermal DSC experiments and is shown in figure 4.

With the content of CaCO$_3$ increase, the broad exothermic peak of cross-linking between unsaturated polyester and styrene widen and the cross-linking curing rate decreases, accompanied with lower curing reaction heat. Therefore, it is revealed that the cross-linking of UPR was retarded by CaCO$_3$, which could improve the mechanical properties of CaCO$_3$/LDUPR samples [25, 26].

#### 3.3.2. Mechanical enhancement of CaCO$_3$ particles

A fundamental principle, which dislocation motion was under constraint of grain boundary resistance with an external force, was put forward [27–29]. Under the condition, mechanical strengthening of fine grain for sample became more pronounced. Hall-Petch formula [30, 31] describes the strengthening principle as:

$$\Delta R_G = K_G d^{-1/2}$$  \(1\)

Where $\Delta R_G$ is the strengthening increment, $K_G$ is the constant, and $d$ represents the particle diameter. It is evident that smaller particle size produced stronger mechanical strengthen for sample. Therefore, combined with orthogonal experiment results above, it is deduced that A-CaCO$_3$, which owned the smallest particle size, performed the strongest mechanical strengthen for CaCO$_3$/LDUPR composites compared with B-CaCO$_3$ and C-CaCO$_3$.

#### 3.3.3. Ripples formation and mechanical enhancement

Sections of UPR, LDUPR, and A-CaCO$_3$/LDUPR cured samples are shown in figure 5. Figures 5(a)–(c) illustrate that cured UPR presents flat morphology with micro cracks and micro voids. Figures 5(d)–(f) shows that there are few ripples in the resin matrix of LDUPR sample as there is no CaCO$_3$ in LDUPR. Figures 5(g), and (h) shows that there are homogeneously distributed bubbles and regular ripples in resin matrix of the cured LDUPR sample with 25.00 phr A-CaCO$_3$, where the specific compressive strength of the sample was 41 percent higher than that of LDUPR sample. The specific formation of ripples and the enhancement of ripples to CaCO$_3$/LDUPR composite, which were not declared before, were explored.

During the curing process of UPR without the presence of CaCO$_3$, the viscosity of resin glue increased accompanying the cross linking between unsaturated polyester and styrene, self-polymerization of styrene, and the vaporization of styrene. Homogeneous resin glue gelled and then cured into solid exhibiting micro voids and micro cracks in the matrix of sample.

Fine particles of CaCO$_3$ immersed and heaped in resin glue, which could be described as ‘CaCO$_3$ reefs’ in resin glue. These ‘CaCO$_3$ reefs’ moved freely in resin glue but became obstacles of glue fluid when resin glue viscosity had suddenly increased. During the process, resin glue fluid swashed against the ‘CaCO$_3$ reefs’, and tiny
waves appeared around these ‘CaCO3 reefs’ during the stick-flow motion of resin glue. After that, ripples generated in the resin matrix till resin cured (see figure 6(a)). Ripples were achieved in the cured resin matrix of sample and they improved the mechanical property of sample. More ‘CaCO3 reefs’ were in resin glue with the content of CaCO3 increasing, and more ripples generated in cured resin matrix.

Figure 6(b) indicates that exceed content of CaCO3 acted as more ‘CaCO3 reefs’ in resin glue for 30.00 phr A-CaCO3/LDUPR composite sample, where ripples were extruded and broken to ‘piece ripples’. It is disadvantageous to the mechanical enhancement of CaCO3 in composite. Therefore, the specific compressive strength of 30.00 phr A-CaCO3/LDUPR composite was 25.15 ± 1.20 MPa · cm³ · g⁻¹. These changes
presented specialties of fine grain CaCO$_3$ incorporated into unsaturated polyester resin and CaCO$_3$/LDUPR composite, performing its unusual mechanical enhancement.

3.3.4. Dimples formation and mechanical enhancement

In smaller scale, dimples are obvious in resin matrix, shown in figure 5(i). As viewed from this smaller scale in the preparation, resin glue fluid streamed around fine particles of CaCO$_3$ and particles parted the fluid stream, which are illustrated in figure 7. At a high value of viscosity, resin glue fluid flowed around particles of CaCO$_3$. 

Figure 4. Non-isothermal DSC curves of a wherein (a) pure UPR, (b) UPR with 10.00 phr A-CaCO$_3$, (c) UPR with 25.00 phr A-CaCO$_3$, (d) UPR with 30.00 phr A-CaCO$_3$; b wherein (e) UPR with 10.00 phr B-CaCO$_3$, (f) UPR with 25.00 phr B-CaCO$_3$, (g) UPR with 30.00 phr B-CaCO$_3$; c wherein (h) UPR with 10.00 phr C-CaCO$_3$, (i) UPR with 25.00 phr C-CaCO$_3$, (j) UPR with 30.00 phr C-CaCO$_3$. 

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and gradually moved slowly. After that, dimple with sharp edge flow generated along with resin glue being cured. During the process, a constant stream moved ahead and mingled with another stream caused by another particle of CaCO₃. Two constant streams flowed through the resin glue gently with distinguished boundaries left, and dimples generated (shown in figure 5(i)). Therefore, the specific dimple exhibited an image of branch divided from trunk of a tree in the cured resin matrix. In accordance with this pattern, one main dimple mingled with several other dimples and generated a typical ductile dimple pattern in which a main dimple being branched into several small dimples.

In light of these extraordinary microstructures of ripples and dimples, major force transmitted along the microstructure, changed its propagation direction against the along dimples. Accordingly, resolution of external force occurred, and the major force was consumed by regular ripples and dimples in resin matrix, resulting in the improvement of compressive strength of the sample. This innovative force resolution mechanism is described in figure 8.

4. Conclusions

Three kinds of fine grain CaCO₃ in different particle sizes were used to prepare CaCO₃/LDUPR composites in this study and their evident mechanical enhancement of on CaCO₃/LDUPR composites was investigated. The finest grain A-CaCO₃ performed the most outstanding actions, including the lowest viscosity effect, the best bubble distribution and the most excellent mechanical strengthening among three kinds of fine grain CaCO₃. Under the optimal conditions of 25.00 phr A-CaCO₃ and 2.50 phr NH₄HCO₃ at 76.0 °C, A-CaCO₃/LDUPR exhibited the lowest apparent density was 0.53 ± 0.02 g · cm⁻³, the compressive strength of 20.27 ± 0.51 MPa, and the highest specific compressive strength of 38.25 ± 1.43 MPa · g⁻¹ · cm³.

The cross-linking between unsaturated polyester and styrene was hindered by CaCO₃ and the exothermic heat of the polymerization was decreased. Unusual matrix microstructure with regular ripples and dimples in CaCO₃/LDUPR composites was presented and explored. It is deduced that resin glue fluid swashed against the ‘CaCO₃ reefs’ and tiny waves appeared around these ‘CaCO₃ reefs’ during the flow motion of resin glue. In smaller scale, resin glue fluid streamed around particles of CaCO₃ and particles parted the fluid stream. Several constant streams flowed through the resin glue gently and mingled with other streams exhibiting an image of branch divided from trunk of a tree in the cured resin matrix. With the extraordinary microstructure of ripples

![Figure 5. SEM micrographs of UPR (a)–(c), LDUPR (d)–(f), and 25.00 phr A-CaCO₃/LDUPR (g)–(i) cured samples.](image-url)
and dimples, major force transmitted along and changed its propagation direction against the ripples starting and was resolved into several components along dimples. Under the regulation mechanism, resolution of external force was carried out and major force was consumed by regular ripples and dimples, which resulting in an improvement of mechanical enhancement of CaCO$_3$/LDUPR composites.

Figure 6. Ripples formation mechanism (a) schematic diagram of ripples in cured resin matrix, (b) schematic diagram of more ’CaCO$_3$ reefs’ and more ripples.

Figure 7. Dimples formation mechanism schematic diagram.
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Conflict of interest statement

The authors declared that they have no conflicts of interest in this work.

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