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Enhanced Mechanical Performance for Nacre-Inspired Polyimine Composites with Calcium Carbonate Particles

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ABSTRACT. Polyimine is a novel functional thermoset material with several attractive functions. Yet the mechanical properties of polyimine-based composites have been rarely investigated. In this work, calcium carbonate (CaCO₃), a cheap and commonly used reinforcing material, has been chosen as the reinforcing filler to form composites with polyimine through heat-pressing under mild conditions to mimic natural nacre. Elemental mapping shows that CaCO₃ particles are evenly distributed in the continuous network of the polyimine matrix. Then thermal analyses and mechanical measurements of hardness, tensile strength, toughness, bending strength, and impact strength have been conducted to characterize the properties of the resultant polyimine composites. The fracture surfaces of the specimens after tensile testing have also been examined by scanning electron microscopy (SEM). The polyimine composites with CaCO₃ particles demonstrate remarkable enhancement on multiple mechanical features, especially on tensile properties. More importantly, the polyimine composites fabricated with 6 wt% of CaCO₃ particles show simultaneous increases of tensile strength and toughness, which are 56% (from 35.75 to 55.79 MPa) and 110% (from 112.82 to 236.54 MJ/m³) respectively in comparison with the polyimine matrix. The work presented herein affords a facile and low-cost approach to enhance the mechanical properties of polyimine material for more practical applications.

Introduction. Reinforced polymer composites have attracted broad interest in recent years owing to their enhanced performance compared to the respective polymer matrix [1-10]. To this end, fillers such as calcium carbonate, zirconia, hydroxyapatite, have been added at low content to various polymers [11], and the resultant composites have demonstrated superior mechanical properties to meet different industrial demands [12]. Polyimine, also called Schiff base polymer, is a novel thermoset material with advantages of self-healing, recyclability and environmental friendliness. Moreover, such a material is often malleable at ambient conditions, holding a good promise for a range of industrial applications including automobile, electronics, medical, etc. [13-19]. However, reinforced polyimine composite has been rarely explored.

Nacre, composed of inorganic particles (mainly of calcium carbonate, CaCO₃) and biopolymers, is widely considered as a gold standard for the engineering of bionic composite with excellent strength and toughness [20]. It has been proposed that the CaCO₃ platelets in natural nacre function to deflect cracks and mitigate localized stress [20]. Hence, a variety of polymer composites reinforced by CaCO₃ particles have been prepared, which have exhibited remarkable improvements in mechanical properties such as tensile strength, stiffness, impact strength, bending strength and toughness [11, 12, 21-27].

Inspired by natural nacre, we have envisioned that CaCO₃ can be used as the reinforcing phase to enhance the mechanical performance of polyimine. Herein, the polyimine composites with varied contents of CaCO₃ have been fabricated by heat-pressing the mixed powder of polyimine and CaCO₃ particles. The resultant composites formed by imine metatheses have demonstrated simultaneous

enhancements for both tensile strength and toughness, which are 56% and 109% respectively for the composite with 6% of CaCO₃. A different optimal level of CaCO₃ particles is required to achieve best performance for bending and impact resistance. The possible reinforcing mechanism is also discussed.

Materials and Methods

Experimental material. All the chemicals including terephthalaldehyde, diethylenetriamine, and triethylene tetramine were purchased from Aladdin Industrial Inc. (China). CaCO₃ was purchased from Sinopharm Chemical Reagent Co., Ltd (China). All reagents were used as received without further purification.

Preparation. The polyimine (PI) matrix was synthesized with terephthalaldehyde, diethylenetriamine, and triethylene tetramine according to the literature [18]. The obtained PI was milled into powder by pulverizer (QE-100, Yili Ltd., China), and then sifted by an 80-mesh sieve. The PI powder and CaCO₃ particles were mixed by a ball miller for 1 hour. Then the mixed powders were heat-pressed by a thermocompressor (JYP-20) under 9 MPa at 80 °C to form polyimine composites.

Characterization. A Rockwell hardness meter (XHQ-150, Shanghai, China) was used to measure the hardness. Tensile tests and bending tests were performed with a Universal Testing Machine (Instron 1121, UK) according to ASTM standard D638 and D5023, respectively. The effective dimension for tensile test sample is 5 x 2 x 2 mm and the effective dimension for bending test sample is 35 x 5 x 4 mm. The crosshead speed for tensile tests and bending tests is 1 mm/min. The toughness was calculated by integrating the area of stress-strain curves. The impact strength was measured on a Charpy impact tester (XJ-40A, Wuzhong, China) with effective sample dimension of 35 x 5 x 4 mm. All the mechanical tests were carried out at room temperature. The average of at least 3 independent measurements was obtained for all mechanical characterization and the P value was calculated by the Student's *t*-test.

The differential scanning calorimetry (DSC) measurement was performed with a DSC instrument (Q20, TA, USA) in the temperature range of 30-150 °C at a heating rate of 5 °C /min. The thermogravimetric analysis (TGA) was conducted with a thermogravimetric analyzer (Q600, TA, USA) in the temperature range of 23-800 °C at a heating rate of 10 °C /min.

Morphology characterization and elemental mapping. The tensile fracture surfaces of PI matrix and composites were observed by a scanning electron microscope (XL-30 ESEM FEG, FEI, USA). The elemental mapping was performed on Genesis 2000 (EDAX Company).

Results and Discussion. The polyimine (PI) was synthesized according to the literature [18]. The sizes of PI powder and additive CaCO₃ particles were measured as about 122±21 μm and 1.2±0.4 μm in diameter by Scanning Electron Microscopy (SEM) (Figure 1b and 1a). The PI composites with calcium carbonate (CaCO₃) particles (PI-CC) were prepared by heat-pressing (80 °C, 9 MPa) the mixed powder of PI and CaCO₃ particles (Figure 1e). The weight percentages of CaCO₃ particles in the composites were 3%, 6%, 9%, 12% and 15%, which were subsequently denoted as PI-CC-3, PI-CC-6, PI-CC-9, PI-CC-12, and PI-CC-15 respectively. The original fracture SEM micrograph and elemental mapping micrograph were performed to verify the distribution of CaCO₃ particles in the PI matrix (Figure 1c and 1d, the image was obtained with PI-CC-6). The yellow and green dots in the mapping graph (Figure 1d) represent calcium (corresponding to CaCO₃) and nitrogen (corresponding to PI), respectively. SEM image of the fracture surface (Figure 1c) shows there are smooth areas with clear boundaries, among which rough areas exist. Comparing the SEM image with the corresponding elemental mapping graph, (Figure 1d) it is found the smooth areas contain only the PI, while the rough areas consist of both PI and CaCO₃. The existence of pure PI areas suggests that the CaCO₃ particles can hardly penetrate into the PI powders during the heat-pressing. The distribution of CaCO₃ particles among the pure PI areas proves that these particles work as the fillers in the composite matrix as our expectation.

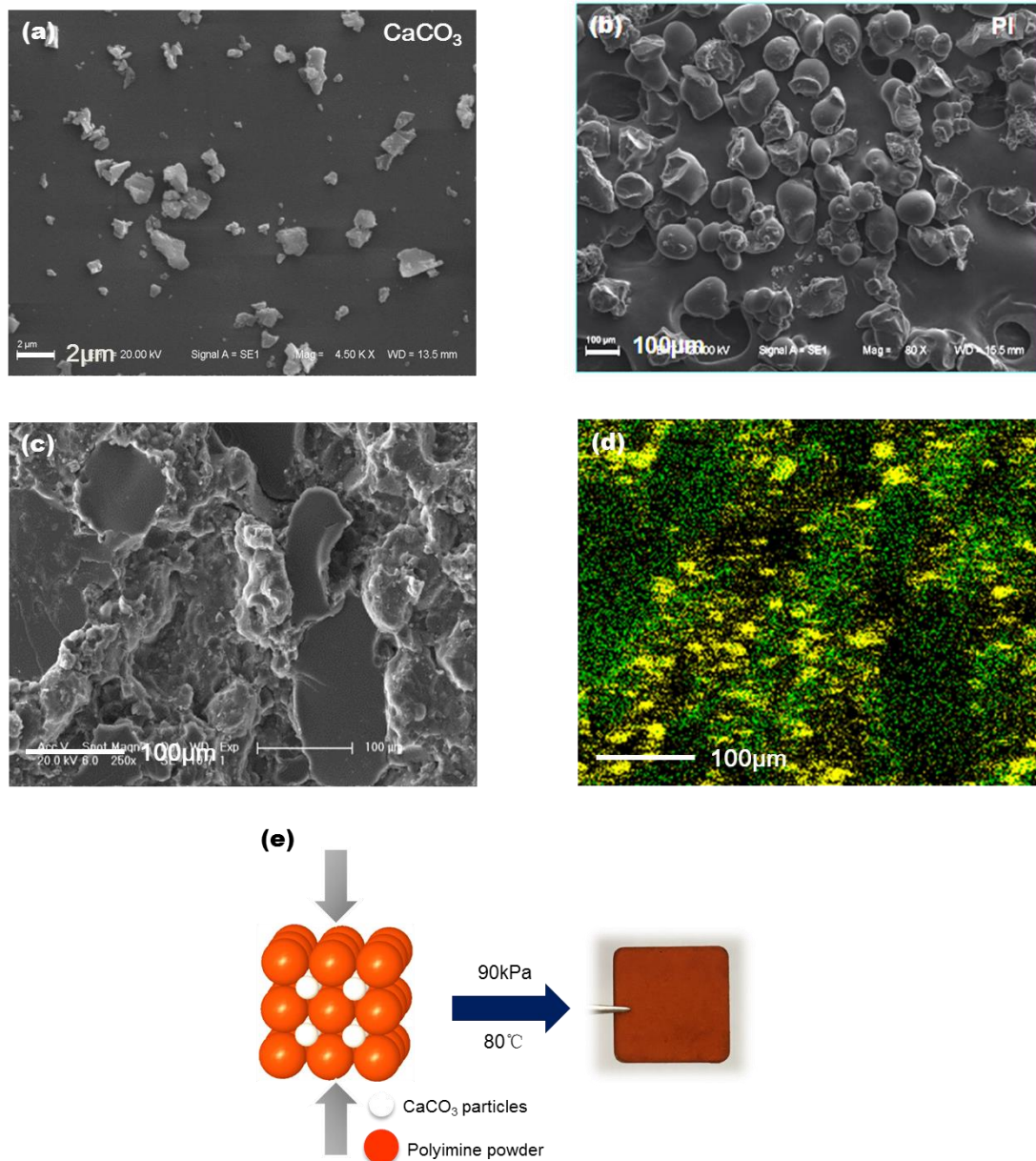


Fig. 1. SEM micrographs of raw materials powder including CaCO_3 particles (a) and PI (b). Fracture SEM micrograph (c) and elemental mapping (d) of Ca and N for the PI composite filled with 6 wt% CaCO_3 particles. The yellow and green dots in (d) represent calcium and nitrogen, which indicate distribution of CaCO_3 particles in the composite of PI-CC-6. Schematic illustration for preparing PI composite is shown in (e).

Next, a range of mechanical measurements including hardness, tensile, bending, and impact strengths have been conducted to characterize the CaCO_3 -enhanced PI composites together with the control of PI matrix. It has been found that introducing CaCO_3 into PI matrix results in little change of the overall hardness as the hardnesses of the composites remain comparable to that of the PI matrix (Table 1).

The tensile property measurement for the PI composites reveals a similar trend with a maximum value at 6 wt% of CaCO_3 particles in terms of tensile strength, toughness, tensile modulus, and elongation at break (Figure 2 and Table 1). Specifically, the tensile strength exhibits a gradual increase from 35.75 MPa for the PI matrix to 55.79 MPa for the PI composite with 6 wt% of CaCO_3 particles, which has been enhanced by 56% (Figure 2a and Table 1). Meanwhile, the toughness has also shown an increase of 109% from 112.82 MJ for the PI matrix to 236.54 MJ for the PI composite with 6 wt% of CaCO_3 particles (Figure 2b and Table 1). Increasing the CaCO_3 content beyond 6% results in a decline

of tensile performance. The enhancement of tensile strength and toughness is significant ($P < 0.05$) for most pairwise comparison among the samples (Figure 2c). It's worth noting that for most composite materials, it is hard to achieve simultaneous improvements on tensile strength and toughness [28, 29]. Yet the PI composite with 6 wt% of CaCO_3 particles exhibits an excellent integration of tensile strength and toughness showing the peaks for both. The rationale underlying such an interesting finding requires further investigation.

The fracture surfaces of the PI matrix and the reinforced composites were examined by scanning electron microscopy (SEM) to reveal the possible rationale for the observed trend in tensile property measurement (Figure 3). Overall, “river-pattern” streaks can be observed in the micrographs of all these samples, suggesting a nature of brittle fracture. Moreover, the micrographs of the composites (Figure 3b-3d) exhibit some granules, which are likely to be CaCO_3 particles, since they are absent in the image of the PI matrix (Figure 3a) and more granules can be found as the content of CaCO_3 in the composite increases. In particular, the micrograph for PI-CC-15 (Figure 3d) shows a rougher surface covered by the granules, suggesting that high level of CaCO_3 content may cause the agglomeration of CaCO_3 [27] and therefore result in markedly reduced tensile strength and toughness as shown in Figure 2.

Table 1. Mechanical properties for PI and PI composites with CaCO_3 .

Samples	Tensile Strength (MPa)	Toughness (MJ/m^3)	Tensile Elongation at Break (%)	Tensile Modulus (MPa)	Bending Strength (MPa)	Bending Modulus (MPa)	Bending Elongation at Break (%)	Impact strength (KJ/m^2)	Hardness (HRR)
PI matrix	35.75 ± 0.86	112.82 ± 14.47	6.31 ± 0.81	559.86 ± 21.01	44.20 ± 1.17	2158.00 ± 30.33	2.03 ± 0.10	6.87 ± 0.43	121.30 ± 1.80
PI-CC-3	44.23 ± 1.27	176.65 ± 1.00	7.99 ± 0.18	606.88 ± 47.72	52.70 ± 1.77	2217.50 ± 78.05	2.48 ± 0.22	6.48 ± 0.21	124.23 ± 0.67
PI-CC-6	55.79 ± 3.77	236.54 ± 49.03	8.47 ± 1.15	720.49 ± 17.16	42.13 ± 0.92	2236.67 ± 15.28	2.03 ± 0.05	6.54 ± 0.75	123.93 ± 0.67
PI-CC-9	46.53 ± 2.67	161.11 ± 6.88	6.93 ± 0.10	694.38 ± 39.79	41.10 ± 4.24	2686.67 ± 28.87	1.85 ± 0.07	7.78 ± 0.11	122.38 ± 0.50
PI-CC-12	40.25 ± 0.21	160.24 ± 6.64	7.96 ± 0.29	531.27 ± 9.92	41.05 ± 5.66	2732.50 ± 38.62	1.85 ± 0.21	5.67 ± 0.31	122.93 ± 0.22
PI-CC-15	28.51 ± 4.35	75.33 ± 29.29	5.17 ± 1.17	569.28 ± 12.71	28.87 ± 0.31	2536.67 ± 55.08	1.20 ± 0	6.16 ± 0.21	121.15 ± 0.88

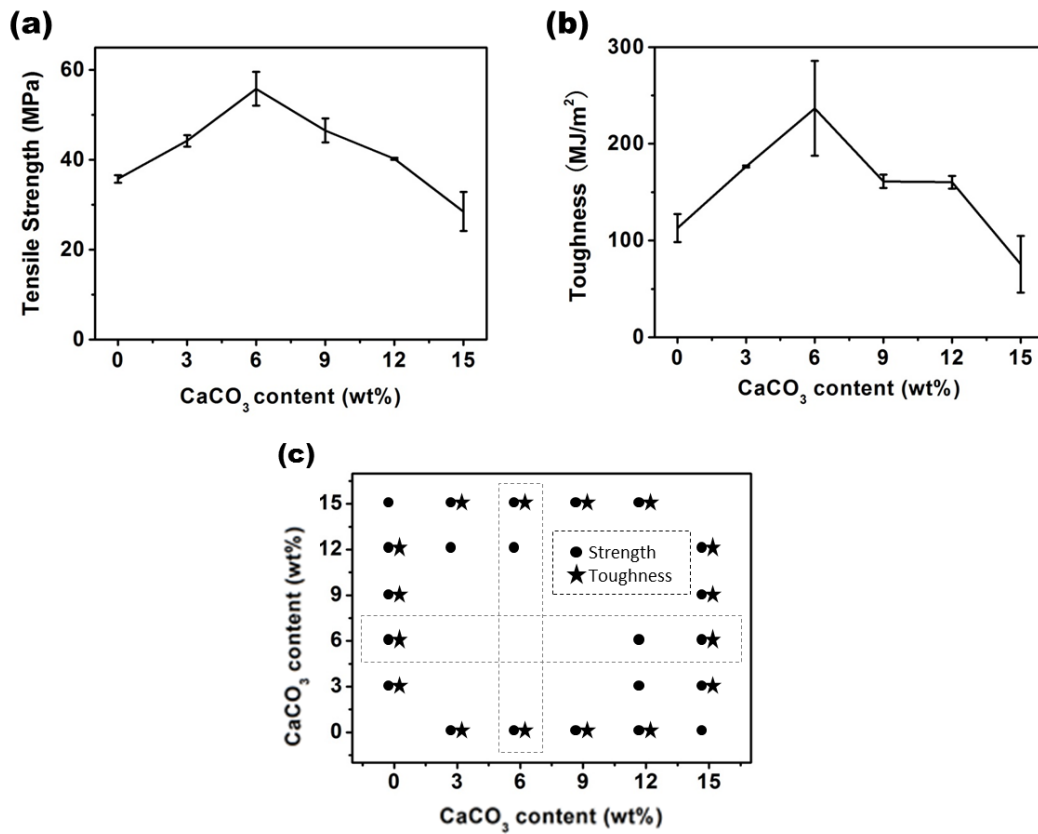


Fig. 2. The tensile strength (a) and toughness (b) of PI composites with different CaCO₃ contents. Both tensile strength and toughness show a maximum value at the CaCO₃ content of 6 %. The statistical significance ($P < 0.05$) for the pairwise comparison of tensile strength (dots) and toughness (stars) among the PI composites with different CaCO₃ contents (c). The dotted boxes highlight the significance of property enhancement for the composite with CaCO₃ content of 6%.

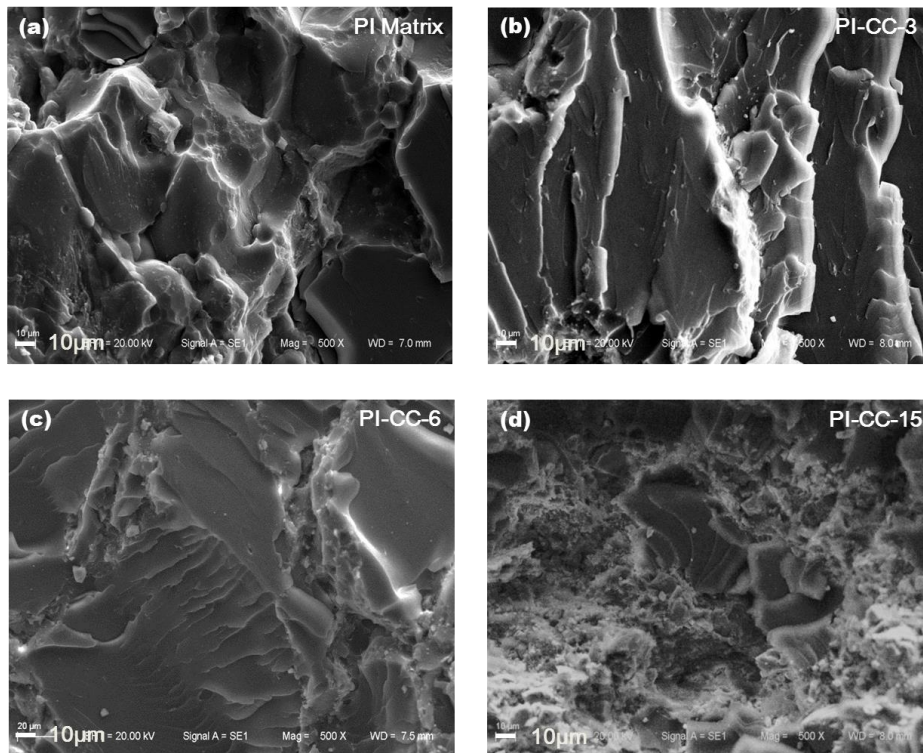


Fig. 3. SEM micrographs of PI (a) and PI composites with various contents of CaCO₃: 3% (b), 6% (c), and 15% (d).

It should be noted that the maximum for tensile modulus and elongation at break also coincide at the composite of PI-CC-6 (Table 1), which agrees with the observation for tensile strength and toughness. Together, the results of tensile property measurement and SEM imaging indicate that a low level of CaCO_3 particles, likely around 6%, can yield a better dispersion in the PI matrix without evident agglomeration and lead to more interfacial interaction between the matrix and the filler. As a consequence, the composite of PI-CC-6 demonstrates the highest tensile performance among the PI composites evaluated. As suggested by previous reports of artificial nacre [20], it is proposed herein that the CaCO_3 particles, when added to the matrix at an optimal amount, can function to disperse localized stress by crack deflection and prevent slippage by mineral bridging.

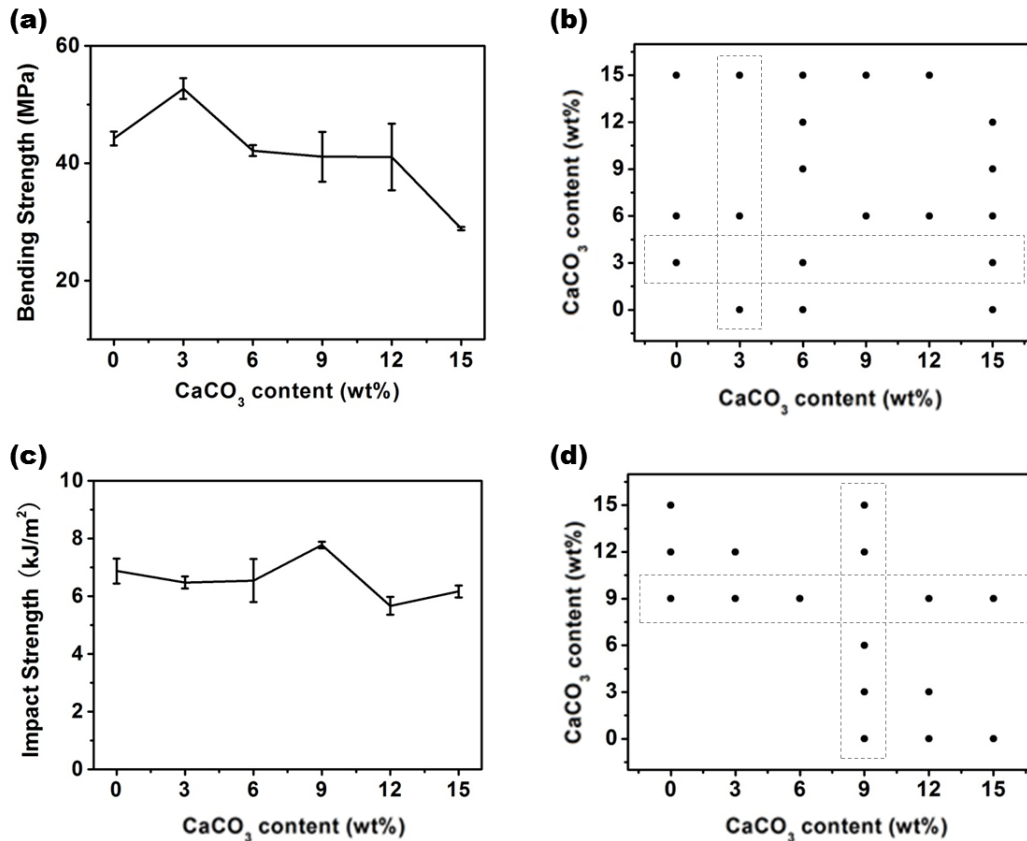


Fig. 4. The bending strength (a) and impact strength (c) of PI composites with different CaCO_3 contents show maximum values when CaCO_3 content is 3% and 9%, separately. The statistical significance ($P < 0.05$) for the pairwise comparison of bending strength (b) and impact strength (d) among the PI composites with different CaCO_3 contents. The dotted boxes in (b) and (d) highlight the significance of property enhancement for the composite with CaCO_3 content of 3% and 9% for bending strength and impact strength respectively.

Furthermore, the bending strength and impact strength of the PI composites with CaCO_3 particles were measured to see whether these properties can also be enhanced. The bending strength displays a peak value for PI-CC-3 (Figure 4a), whereas the impact strength shows a maximum for PI-CC-9 (Figure 4c). The increases are 19% for bending strength (from 44.2 MPa for the PI matrix to 52.7 MPa for PI-CC-3) and 13% for impact strength (from 6.87 kJ/m^2 for the PI matrix to 7.78 kJ/m^2 for PI-CC-9) (Table 1). The significance of the pairwise comparison for bending strength and impact strength is shown in Figure 4b and 4d respectively. These results suggest that a different optimal level of CaCO_3 particles is required to achieve best performance for these mechanical properties. Due to the rigid nature of CaCO_3 particles, it is reasonable that less CaCO_3 particle is needed to obtain the

optimal bending strength and more for the optimum of impact resistance, compared to the tensile enhancement. Yet, the reinforcing mechanism is possibly similar to that of tensile enhancement, i.e. by crack deflection, interlocking and mineral bridging. It should be noted that, similar to the case of tensile properties, over-dosing use of CaCO_3 particles also results in a decline of bending and impact resistance, likely also because of agglomeration of CaCO_3 particles.

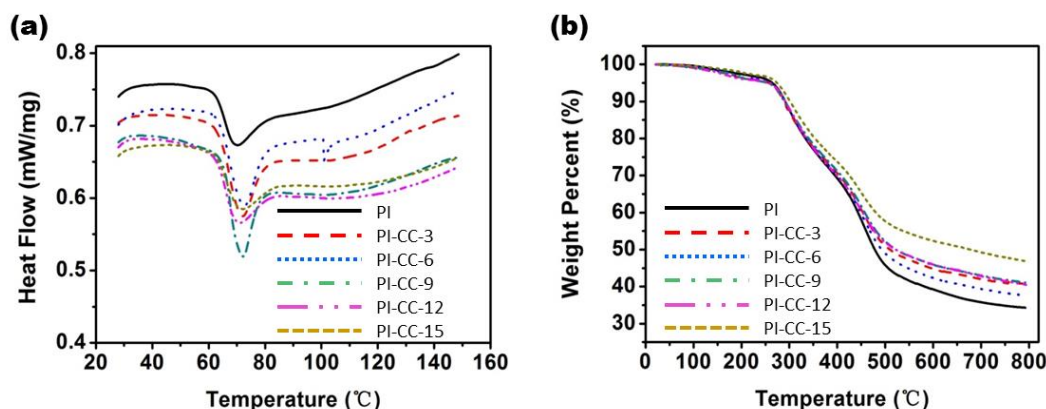


Fig. 5. The DSC (a) and TGA (b) curves of PI matrix and PI composites with various CaCO_3 contents.

Thermal analyses of differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed to assess the thermal properties of the composites (Figure 5). Addition of CaCO_3 particles incurs a slight increase on the glass transition temperature (T_g) of the PI composites compared to the matrix (from 62 °C to 65 °C) in DSC plots (Figure 5a). Figure 5b shows the weight loss of various samples with increasing temperature. The PI matrix and composites initiate degradation at similar temperature. Yet, the PI composites with more content of CaCO_3 particles (e.g. PI-CC-15) retain higher weight percentage under the temperature higher than 400 °C, which may be contributed by two factors. First, CaCO_3 is thermally stable till 800 °C. Thus the PI composite containing higher weight percentage of CaCO_3 particles will result in more inorganic residuals. Second, the dispersed CaCO_3 particles could also enhance the thermal stability of PI composites via a mechanism of heat buffering and re-distribution.

Summary. Inspired by natural nacre, a series of PI composites filled with CaCO_3 particles have been successfully prepared under mild conditions. The resultant composites demonstrate a range of mechanical enhancements including tensile strength, toughness, bending strength, and impact strength, which are 56%, 109%, 19%, and 13% at the respective maximum values, compared to the PI matrix. Interestingly, simultaneous improvements of tensile strength and toughness have been observed for the PI-CC-6 composite, indicating an excellent balance of tensile strength and toughness reinforcement at the optimal amount of CaCO_3 . Yet, lower level of CaCO_3 content is required to achieve the best bending performance and higher level for impact resistance, suggesting that an optimal content shall be determined base on the individual case of application. Furthermore, the incorporation of CaCO_3 particles can also enhance the thermal stability of the PI composites. Together, this work demonstrates that the mechanical properties of PI matrix can be enhanced by CaCO_3 particles, affording a facile and low-cost approach to reinforce PI for more applications.

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