Preparation of pineapple leaf micro crystalline cellulose loaded boron nitride powder in presence of polydopamine

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Abstract: The surface of hexagonal boron nitride (h-BN) was modified by polydopamine (PDA) where water being used as the dispersion medium. The interaction between h-BN and pineapple leaf micro crystalline cellulose (PLMCC) was improved resulting in a PDA@h-BN-PLMCC composite powder. This facilitates interactions between h-BN and PLMCC, aligns the h-BN layers along the direction of the cellulose, and eliminates anisotropy. This novel composite powder has potential application for areas such as new thermal interface materials and protection materials for wearable devices.

1. Introduction
Boron nitride (BN) can be classified into four categories according to geometric structures: cubic BN, hexagonal BN, rhombohedral BN, and wurtzite BN. Hexagonal boron nitride (h-BN), which lattice structure is close to that of graphite (also known as white graphite), has attracted much attention. h-BN offers excellent chemical and temperature stability, high conductivity, and good dielectric properties. So h-BN has been widely used in modification of other resin materials [1-3]. However, the surface of the boron nitride layer is relatively inert, which prevents its interaction with resin substrates. In addition, the nano sheets of h-BN lamella are stacked loosely leading to thermal resistance. Therefore, it is critical to study and resolve this key issue.

Cellulose is a degradable and very abundant natural polymer. Due to the rapid consumption of non-renewable resources, it is critical to develop renewable cellulose products. Micro crystalline cellulose (MCC) is obtained through hydrolysis of natural cellulose by strong acid; it has the basic structure and properties of cellulose. Moreover, its structure results in special chemical and physical properties such as a high modulus, high specific surface area, high strength, and high transparency [4-6].

Currently, many abandoned pineapple leaves are produced near coastal areas. Hence, making full use of discarded pineapple leaves would create a value-added agricultural waste and promote regional
economies. This would also conserve sources and prevent pollution. For example, dos Santos et al prepared nano crystalline cellulose with high crystallinity and high thermal stability from discarded pineapple leaves [7]. The average length was 249.70±51.50 nm, and the average diameter was 4.45±1.41 nm. Another type of cellulose crystallites with high crystallinity and low thermal stability were prepared from soft wood pulp by Zhao et al, who also developed a nano paper with high transparency [8]. It is also possible to functionalize pineapple leaf cellulose due to its unique structures and properties, then probably interacting with h-BN. For example, Xia et al combined sisal fiber cellulose with h-BN, and the composite was filled with epoxy resin to produce a thermally conductive composite material [9]. Nano crystalline cellulose was combined with BN and MoS\textsubscript{2} by Li et al to prepare an anode for flexible cationic batteries [10]. However, research on the use of pineapple leaf micro crystalline cellulose (PLMCC) combined with BN for surface modification and dispersion is rare.

Hence, we aimed to modify BN surface with polydopamine (PDA). This was combined with PLMCC via a pulsed ultrasonic method to form an environmentally friendly composite powder. A new method of loading h-BN to PLMCC was also developed.

2. Technical details

2.1. Materials and Synthesis procedure

h-BN (10 μm) was obtained from Qingzhou Fangyuan Boron Nitride Factory (≥99%). Dopamine (DA) hydrochloride (≥98%) and tris(hydroxymethyl)-aminomethane hydrochloride (Tris, ≥99%) were purchased from Macklin. Poly(vinyl alcohol) was purchased from Changchun Chemical Co. LTD (≥99%). The MFC was prepared in the laboratory.

Tris (0.605 g) was dissolved in 500 mL deionized water, and the pH of the solution was adjusted to 8.5[11]. h-BN (2.000 g) was added to the solution, further stirred and sonicated at 60 °C and 600 W using the ultrasonic signal transmitter (NH-1000) obtained from Shanghai Hanuo Instrument for 3 h so that the h-BN sheets were stripped. DA-HCl (0.200 g) was then added to the mixture with continued stirring and sonication for 3 h so that the dopamine would polymerize and fully interact with the h-BN surface. After the reaction was complete, the mixed solution was subjected to vacuum filtration and washed with deionized water (50ml each time, 5–6 times) until the pH was neutral. The mixture was then dried at 80 °C for 24 h to form PDA@h-BN.

PDA@h-BN (0.700 g) and PLMCC (0.200 g) were mixed and dispersed in distilled water (300 mL). The solution was ultrasonicated at 60 °C and 600 W for 5 h with ultrasonic pulse time of 2s. The mixture was then treated with suction filtration and dried to form PDA@h-BN-PLMCC.

2.2 Characterizations

The SEM with a tungsten filament (ZEISSEVO18) was purchased from Carl Zeiss (Germany). The thermal analyzer (TGA2) was obtained from Mettler-Toledo Instruments (US), and the X-ray photo electron spectrometer (ESCALAB250Xi) was purchased from Thermo Fisher Scientific (US).

3. Results and Discussion

Fig.1 shows the route that was followed to modify h-BN with PDA. h-BN contains a six-membered ring composed of alternating B atoms and N atoms with π-π conjugation. Dopamine is prone to nucleophilic reactions, inter molecular rearrangements in weak bases environments; thus, there is oxidative polymerization of dopamine on the surface of h-BN [12]. The attachment of PDA to the surface of h-BN is attributed the vander Waals forces between the two as well as the benzenering structure of the PDA.
Figure 1. Schematic process of surface modification of h-BN with PDA

Fig.2(a) shows that h-BN suspended and agglomerated on interface of water because of its inert surface; the hydrophilic phenolic hydroxyl and amino groups in PDA facilitates dispersion and stabilization of PDA@h-BN in water[13]. The elemental compositions of h-BN and PDA@h-BN were measured by XPS as shown in Fig. 2(b) and Table 1. The two main peaks in the broad spectrum of h-BN corresponding to N1s (397.1 eV) and B1s (189.2 eV); the peaks of O1s (531.8 eV) and C1s (284.7 eV) were relatively weak. The content of N and B were 47.76% and 46.65%, respectively; C was only 4.99%. The contents of N and B in PDA@h-BN were 38.13% and 40.27%, respectively. The total content of N decreased, while the C increased to 18.36% because PDA contains more C atoms than N atoms. The peaks in the XPS spectrum of pBN were curve-fitted, and the chemical bonds corresponding to the peaks at 284.6 eV, 285.4 eV, and 288.3 eV were -CH-, C-N/C-OH, and C=O/COOH, respectively. The C-N and C=O groups were from PDA, which further demonstrated the successful binding of PDA to h-BN. As shown in Fig.2(c), PDA@h-BN showed similar weight loss as that of DA-HCl. The rate of weight loss began to increase after 215 °C, and the final weight loss was 3.47%. This indicates that PDA@h-BN is stable below 215 °C. The amount of PDA on PDA@h-BN was estimated to be 2.77%.

Figure 2. (a) Images of PDA@h-BN and h-BN dispersed in water; (b) XPS survey scan for h-BN and PDA@h-BN and C 1s high-resolution spectra for PDA@h-BN; and (c) TGA curves of h-BN, PDA, and PDA@h-BN
Table 1. Summary of XPS measurement results of h-BN and PDA@h-BN

| Sample          | C 1s | O 1s | N 1s | B 1s | O/B | O/B |
|-----------------|------|------|------|------|-----|-----|
| h-BN            | 4.99 | 0.58 | 47.76| 46.65| 0.10| 0.01|
| PDA@h-BN        | 18.36| 3.23 | 38.13| 40.27| 0.45| 0.08|

SEM image of the unmodified h-BN are shown in Fig. 3(a)—the BN sheets were stacked and irregularly dispersed due to inter molecular forces. Fig. 3(b) shows the SEM image of the self-prepared PLMCC with a smooth surface and a length of 50±10 μm. Many PDA@h-BN were tightly attached to the surface of the PLMCC in Fig.3 (c). This shows that the loading effect of PDA@h-BN is much higher than that of h-BN, which is due to the full contact and interaction of PDA@h-BN with PLMCC under ultrasound. We speculated that the phenolic hydroxyl groups from PDA would form hydrogen bonds with the hydroxyl groups on PLMCC to facilitate binding between PDA@h-BN and PLMCC. The PDA@h-BN-PLMCC composite existed as a fine powder as shown in Fig.3(d). This water-based method for combining PDA@h-BN with PLMCC is environmentally friendly and is a practical and feasible method for the surface treatment, surface activation, and spheroidization of h-BN. The spheroidization of h-BN will be reported in a subsequent study.

Figure 3. SEM image of (a) h-BN, (b) PLMCC, (c) PDA@h-BN-PLMCC, (d) photo of PDA@h-BN-PLMCC powder and (e) FT-IR spectra of h-BN, PLMCC and PDA@h-BN-PLMCC.

The FT-IR spectra of h-BN, PLMCC, and PDA@h-BN-PLMCC are exhibited in Fig. 3(e). The most distinctive peaks, i.e., those at 1372 and 817 cm−1, are attributed to B-N stretching and B-N bending, respectively [14]. The characteristic peaks of PLMCC on the spectrum of PDA@h-BN-PLMCC disappeared nearly completely, while the two characteristic peaks of PDA@h-BN remained, indicating that PDA@h-BN is attached to PLMCC. This is consistent with the
structure in Fig. 3(c).

4. Conclusions

h-BN was modified using PDA to form PDA@h-BN. The measured mass percentage of PDA is ca.1.86% from TG analysis. The PDA@h-BN could be well dispersed in water, and it could be combined with PLMCC under ultrasound. The as-prepared PDA@h-BN-PLMCC composite would be used in the preparation of thermal interface materials, wearable device materials, etc. Future work will identify the experimental conditions for preparing PDA@h-BN and combining it with PLMCC, including a mechanistic understanding.

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