Nitrogen-Rich Perylene Nanosheet Enhanced Bismaleimide Resin

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Abstract: The low toughness of bismaleimide resin (BMI) hinders its application in the aerospace field. In order to improve the strength and toughness of BMI resin simultaneously, this study proposes to introduce perylene-dicyandiamide (P-DCD) nanosheets with an ultra-rigid conjugated planar structure into the polymer matrix of bismaleimide resin through hydrogen bonding and cross-linking to construct modified composites. The research results showed that the modified cured composites exhibited excellent mechanical properties, with a significant increase in impact strength of 135.8%, flexural strength and flexural modulus of 87.1% and 44.6%, respectively. The thermal properties of the resin were maintained before and after modification, with the glass transition temperature (Tg) of 284.0 °C and decomposition temperature > 520 °C. Meanwhile, the strengthening and toughening mechanism of the bismaleimide-based system modified by additive P-DCD were also explored. The results showed that the functional group of dicyandiamide in nanosheets and the hydrogen bonding effect in P-DCD synergically increased the cross-linking network and compatibility between P-DCD and the matrix resin.

Keywords: Bismaleimides (BMI), Composite Material, Toughening, Mechanical Property, Thermal Property.

1. INTRODUCTION

Due to its high strength and stability, advanced composite materials are widely used in various fields such as the electronics industry and aerospace. Polymides are thermos-resistant polymers with imide groups in the main chain, which have been intensively studied since the 1960s for their excellent thermal stability and high mechanical properties, along with their super chemical resistance and electrical properties [1,2]. As a matrix of fiber reinforced plastics or composites, Bismaleimide (BMI) is a new type of thermosetting resin derived from the imide resin system in polyimide-based advanced composites, which not only retains the advantages of high-temperature resistance of polyimide resin, but also have excellent processability, corrosion resistance, low shrinkage, and low creep properties comparable to epoxy resin. Because of its high chemical stability, excellent thermal resistance, good radiation resistance, and low water absorption, it can be used for a long time at 170 °C in a wet environment, and after post-curing treatment, its dry state use temperature can even reach 230 °C~250 °C, [3-5] and it is widely applied in many related industries such as aerospace and electronics industry [6-8]. Additionally, the pristine BMI resin exhibits easy process ability similar to the epoxy resin so the cost of manufacturing was low. However, the conventional BMI resin still has drawbacks such as high brittleness, poor impact resistance, and crack resistance caused by high cross-linking density [9-12]. Therefore, in practical applications, it is crucial to toughen BMI resin while ensuring its excellent inherent properties to support it from significant deformation under high stress. Much research has focused on modifying BMI resin to improve its toughness [13-15].

From a supramolecular and material point of view, coplanarity and rigidity often promote strong intermolecular electronic coupling and reduce the energy barrier for the intermolecular transport of charges, excitons, and phonons, affording advanced materials properties in bulk [16]. Therefore, Perylene-Dicyandiamide (P-DCD) nanosheets can be an ideal filler for advanced composite materials, because of its ultra-rigid conjugated planar structure [17]. Ma [18] introduced a rigid planar 2,5-diphenyl-[1,3,4]-oxadiazole structure with strong intermolecular π–π stacking interactions into the main chain of resins, the corresponding cured resins had high mechanical properties and relaxation temperature. Ding [19] fabricated a modified conjugated molecule curing agent Ethyl Glycidyl Ether-2-Methylimidazole (EGE-2-MI). The epoxy resin system using EGE-2-MI as the curing agent can be efficiently cured at 110-120 °C. This novel moderate-temperature curing system with decent storage life and mechanical properties can overcome the rooted disadvantage of imidazole curing agents.

In this work, we synthesized a new 2D material (P-DCD) based on hydrogen bonding with a large π-conjugated system and nitrogen-rich atoms and used it
as the modified curing agent. P-DCD not only introduced hydrogen bonds, but also changed the cross-linking structure of BMI resin to obtain composite materials with excellent mechanical properties, which provides a promising approach for developing high-performance BMI composite materials.

2. EXPERIMENTAL

2.1. Materials

4,4’-Bismaleimidodiphenyl methane (BMI), dicyandiamine (DCD) and N,N-dimethyl formamide was purchased from Shanghai Macklin Biochemical Technology (Shanghai, China) Co., Ltd. BMI was commercialgrade yellow power containing more than 85% of maleimide double-bond structure. Perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA) was provided by Shanghai Aladdin Biochemical Technology(Shanghai, China) Co., Ltd. 4,4’-(4,4’-Isopropylidenediphenyl-1,1’-Diyl dioxy) Dianiline was received from Shanghai Taitan Scientific Co., Ltd. Ethylene glycol, dichloromethane, acetone and anhydrous methanol were supplied from Chengdu Chron chemical (Chengdu, China) Co., Ltd.

2.2. Synthesis of P-DCD

First, PTCDA (2 g, 5.098 mmol) and DCD (4 g, 47.574 mmol) were dissolved in 40mL N,N-dimethyl formamide and 40mL ethylene glycol solvent, mixed homogeneously, and then fully reacted in the solvent at 200 °C for 60 h. After the reaction was completed, the red solution product was washed several times with a large amount of anhydrous alcohol, dichloromethane, acetone, N,N-dimethyl formamide, and deionized water sequentially to remove the residual reactant. Finally, the samples were freeze dried at -60 °C for 12 h in a vacuum to obtain Perylene-Dicyandiamide (P-DCD) organic nanosheets containing ultra-s rigid conjugated planar structure.

2.3. Synthesis of Dianiline+P-DCD/BMI Resins

Dianiline+P-DCD/BMI thermosets fabricated with various weight ratios of as-synthesized Dianiline, P-DCD and BMI matrix. Firstly, different amounts of P-DCD and dianiline were added to the above BMI and milled and blended uniformly to get the copolymer (donated as X-Dianiline+Y-P-DCD/BMI, where X represents the mass fraction of Dianiline and Y represents the mass fraction of P-DCD).

Afterward, the copolymer was poured into a PTFE mold and cured following the procedures of 100 °C/1h + 180 °C/3h + 200 °C/2h + 260 °C/2h. Finally, the modified P-DCD+Dianiline /BMI resin was cooled down to room temperature and demolded for further testing.

2.4. Characterizations

Structural characterization of P-DCD and resins was studied by Xray diffraction (XRD) patterns, which were recorded on anX’Pert PRO diffract meter using a Ceramic Cu X-ray tube at a scanning rate of 5°/min between 5° and 60°. Solid-state [13] C CP MAS NMR spectroscopy was carried out on a Bruker Avance III TM 600 MHz NMR spectrometer. Fourier transform infrared spectra (FT-IR) were recorded in the region 400 to 4000 cm⁻¹ on a Nicolet-5700 spectrometer.

Figure 1: Synthesis process diagram of Dianiline+P-DCD/BMiresins
(U.S.A) with a resolution of 0.5 cm$^{-1}$. Differential scanning calorimetry (DSC, PE DSC6000, U.S.A) was used to determine the curing property by isothermal (10 K·min$^{-1}$) from 50 °C to 380 °C under N$_2$ atmosphere. The different composite materials were tanked into a DSC aluminum crucible. The morphology of P-DCD was observed by Scanning Electron Microscope (SEM, Ultra55, Germany). The morphology and high-resolution lattice of P-DCD were conducted by transmission electron microscope (TEM, FEI Talos 200X, U.S.A). The impact strength was carried out according to GB/T 1843-2008 (Chinese standard) and measured by an impact testing machine (JJ-15) with the sample dimension of 80 mm $\times$ 10 mm $\times$ 4 mm$^3$.

3. RESULTS AND DISCUSSION

3.1. Structural Characterization of P-DCD

The XRD pattern of P-DCD nanosheets is shown in Figure 2a, with a distinct π-π stacking peak at 2θ = 27.2° corresponding to its lattice spacing of 3.28 Å. Nitrogen-rich group stacking (3.54 Å and 7.73 Å), which demonstrated the successful synthesis of the additive P-DCD. Meanwhile, the XRD pattern of P-DCD displayed high absorption intensity, suggesting that the product synthesized herein has a crystal structure and high purity, proving its crystalline and aggregated state structural features.

The solid-state $^{13}$C NMR spectrum (Figure 2b) was presented to further verify the chemical structure of P-DCD. In Figure 2b, the peaks at 120 to 131 ppm are assigned to the characteristic peaks of the perylene part. The signal at 161 ppm is observed for -C=O group part. The signal located at 164 ppm is attributed to the nitrogen-rich part [20]. According to the above considerate analysis, the results demonstrate that the target product P-DCD was successfully synthesized.

The FT-IR spectra of DCD, PTCDA, and P-DCD were presented in Figure 2c. The absorption peaks at 2207 cm$^{-1}$ and 1639 cm$^{-1}$ are attributed to stretching vibrations of C≡N and C=N in the spectrum of DCD. The characteristic peaks of PTCDA are separately detected at 1772 cm$^{-1}$ for C=O bonds, 1594 cm$^{-1}$ for C=C bonds, and 1022 cm$^{-1}$ for C-O. In comparison with DCD, the stretching vibration peak of N–H bonds at 3121 cm$^{-1}$ moves to the higher wave number, which is caused by the appearance of hydrogen bonding. In the spectrum of P-DCD, the peak corresponding to carbonyl (C=O) stretching vibration, initially positioned at 1772 cm$^{-1}$, changed to 1689 cm$^{-1}$ due to full imidization [21-24]. This spectral signature suggested the disappearance of anhydride (O=C–O–C=O) group and the complete imidization between anhydride (O=C–O–C=O) and amine (-NH$_2$) groups in PTCDA and DCD, respectively. In addition, the slight blue shift in the perylene-ring skeleton vibration peak (C=C, from

Figure 2: Structural characterizations of P-DCD. (a) XRD patterns, (b) $^{13}$C NMR spectra, (c) FT-IR spectrum, (d) SEM image, (e) and (e') TEM images
1594 cm\(^{-1}\) to 1590 cm\(^{-1}\) indicated the enhanced \(\pi-\pi\) stacking [25-27]. Compared with PTCDA, the peak corresponding to the bending vibration of C-H changes from 1302 cm\(^{-1}\) to 1361 cm\(^{-1}\), the characteristic peak C-O (1022 cm\(^{-1}\)) of PTCDA is weakened, and the four peaks at 950-730 cm\(^{-1}\) represent the stretching vibration of C-N and the bending vibration of C-H and N-H.

SEM and TEM images of P-DCD are shown in Figure 2d-e'. It clearly showed that P-DCD formed a regular nanosheet morphology. The above characterization confirmed that P-DCD was successfully synthesized.

3.2. Curing Behavior of Dianiline+P-DCD/BMI Resins

In order to study the changes of chemical structure during the curing process, FT-IR technique was adopted to investigate the possible curing reactions of pure BMI and 0.25 Dianiline +0.1 P-DCD/BMI resin, and the FTIR spectrum is shown in Figure 3a. As shown in Figure 3a, the absorption peaks of located at 2922 cm\(^{-1}\)(C=C) and 2852 cm\(^{-1}\)(C-H) are ascribed to the ring of BMI. At 1699 cm\(^{-1}\) is the characteristic the peak of carbonyl group (-C=O) on the ring of imide, and a band related to the benzene ring at 1511 cm\(^{-1}\). In addition, the BMI showed the absorption bands characteristic of maleimide groups at 1143, 823, and 688 cm\(^{-1}\). The stretching vibration absorption of C-N-C on the maleimide ring at 1143cm\(^{-1}\), the out-of-plane vibration absorption of the C=C double bond on the BMI ring at 823cm\(^{-1}\), and the characteristic absorption peak at 688cm\(^{-1}\) is=C-H [28]. With the proceeding of curing reaction, the characteristic peaks of the N-H at 3749 and 3628 cm\(^{-1}\), as well as C≡N characteristic peaks at 2000cm\(^{-1}\) emerge. The C=O benzene ring, and C-N-C peaks at 1728, 1542, and 1178 cm\(^{-1}\) were weakened in intensity. The characteristic absorption peaks of C=C and =C-H on the maleimide groups at 823 and 688cm\(^{-1}\) are almost disappearing. The above changes indicate that the reaction is essentially complete, suggesting that the curing process is feasible.

The reactions between Dianiline, P-DCD, and BMI resin can be further confirmed by the XRD curves of the composite resins as shown in Figure 3b. The XRD spectra of all composite resins are almost similar to the pure BMI resin. In detail, there are two peaks appearing at 2\(\theta\)=18.3° and 2\(\theta\)=39.1° in the diffraction pattern of BMI resin, whereas the peak at 2\(\theta\)=18.3°gradually becomes progressively sharper and shifts toward smaller angles with increasing the content of Dianiline and P-DCD, reflecting that there is an interaction between Dianiline, P-DCD and BMI resin, and thus producing a loss of regularity with respect to pure P-DCD crystals. Moreover, the characteristic
diffraction peak of P-DCD at $2\theta = 11.4^\circ$ is not observed, indicating that P-DCD is mixed with other components at a molecular level without the formation of P-DCD crystallite.

To further clarify the remarkable curing behavior of Dianiline+P-DCD/BMI resins, the DSC technique was adopted to investigate the possible curing reactions of pure BMI and Dianiline+P-DCD/BMI resins. The DSC curves are shown in Figure 3c, showing similar single exothermic peaks, which indicate that the Dianiline+P-DCD/BMI system reacts homogeneously, and the additives P-DCD and Dianiline have good compatibility with the resin matrix, as the additives contain a large amount of active terminal amino groups. Compared to the $T_g$ value of BMI resin, the addition of dianiline and P-DCD causes $T_g$ to transfer to a lower temperature. The slight decrease in the peak temperature of the 0.15 P-DCD/BMI resins from 293.5 °C to 271.2 °C as compared to the pure BMI is due to the changes in the molecular structure of the polymer induced by the introduction of the dianiline and P-DCD. This may be due to the production of a substance with relatively poor heat resistance, resulting in a slight decrease in the thermal stability of the composite resin. The overall $T_g$ value of this composite resin material is relatively high, exceeding 270°C, and the high $T_g$ ensures its application in high-temperature environments.

In addition, the TGA tests of P-DCD, composite resins, and BMI resin in Figure 3d-f show that the decomposition temperature of the composite resins exceeds 500 °C, it has increased by about 50 °C compared to other literature, indicating that the modified BMI resins maintain good thermal stability. Dianiline+P-DCD/BMI showed similar thermal stability to P-DCD/BMI due to the low amount of added P-DCD and dianiline.

### 3.3. Mechanical Properties of Dianiline+P-DCD/BMI Resins

As can be seen from Figure 4, the addition of modified dianiline and P-DCD organic nanosheets can toughen the BMI resin, and significantly improve the impact strength, flexural strength, and flexural modulus, of which Figure 4 modified dianiline can be added according to the addition of 0.1wt%-0.35wt% can be obtained a better modification effect (when the addition amount of modified P-DCD organic nanosheets is all 0.1wt%), the most significant improvement in the mechanical properties of the composites obtained when modified P-DCD is added to the bismaleimide resin according to 0.25wt%. When 0.1wt% modified perylene dicyanamide organic nanosheets and 0.25wt% modified dianiline were added, the impact strength of the BMI resin composite material increased by 135.8% compared to the matrix, and the flexural strength and flexural modulus were increased by 87.1% and 44.6%, respectively, compared with the pure bismaleimide resin matrix. Figure 5 shows the resin samples with different proportions, through the
novel perylene-based nitrogen-rich organic nanosheets modification and the addition of a certain amount of dianiline, the mechanical properties of the modified BMI resins obtained were significantly improved, and the problems of the bismaleimide cured products showing obvious brittleness and poor fracture toughness were solved.

The schematic diagram of the strengthening and toughening mechanism is exhibited in Figure 6. Due to the dual functional groups of dianiline and BMI, a linear polymer chain without cross-linking is formed. Furthermore, due to the chemical and physical stability of P-DCD nanosheets, which have a stacked structure and are rich in amino groups, individual P-DCD molecules are unable to cross-link BMI, but P-DCD nanosheets [29]. The addition of rigid π-π conjugated P-DCD increased the cross-linking of the polymer chains, the terminated amino groups of P-DCD acted as cross-linked points to generate a tight interface bonding, maintaining the structural integrity of the polymer matrix for strengthening [30-31]. Additionally, redundant dianiline addition tends to accelerate the local excessive cross-linking of modified resins leading to deteriorated mechanical properties of the resin matrix.

4. CONCLUSIONS

In general, novel Perylene-Dicyandiamide (P-DCD) nanosheets with an ultra-rigid conjugated planar structure were synthesized and introduced into the polymer matrix of bismaleimide resin through hydrogen bonding and cross-linking to achieve excellent mechanical performance and desirable thermal performance. The results showed that the functional group dicyandiamide nanosheets and the hydrogen bonding effect in P-DCD increased the compatibility between P-DCD and the matrix resin. P-DCD not only introduced hydrogen bonds, but also changed the cross-linking structure of BMI resin to obtain composite materials with excellent mechanical properties, which provides a promising approach for developing high-performance BMI composite materials.

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REFERENCE

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