Effect of covalent functionalization of multi-walled carbon nanotubes with HDI trimer on mechanical properties of polyaspartate polyurea

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Abstract

To improve the mechanical properties of polyaspartate polyurea (PAEP), functionalized multi-walled carbon nanotubes reinforced polyurea composites (HDIT-MWCNTs/PAEP) were prepared by covalently functionalizing multi-walled carbon nanotubes (MWCNTs) with hexamethylene diisocyanate (HDI) trimer. The dispersibility, wettability and interfacial properties of HDI trimer functionalized MWCNTs (HDIT-MWCNTs) in PAEP were analyzed. The tensile properties of HDIT-MWCNTs/PAEP composites were tested and the reinforcement mechanism revealed. The results showed that compared with the pure multi-walled carbon nanotubes (P-MWCNTs), HDIT-MWCNTs were uniformly dispersed in the matrix and the wettability and interfacial properties were greatly improved. The contact angle of PAEP with HDIT-MWCNTs was 32.92°, a reduction of 46.3% compared with the P-MWCNTs. The interfacial energy and adhesion work between PAEP and HDIT-MWCNTs (25.14 mJ m⁻², 95.47 mJ m⁻²) were 46.7% and 24.2% higher than those of P-MWCNTs. When the content of HDIT-MWCNTs was 0.5 phr, the tensile strength and Young’s modulus of the composites reached a maximum of 17.78 MPa and 170.31 MPa; an increase of 28.4% and 90.8% respectively, compared with pure PAEP. According to the cross-section of HDIT-MWCNTs/PAEP, its strengthening mechanism was mainly manifested by the deflection and bifurcation of cracks and the plastic deformation of PAEP matrix due to HDIT-MWCNTs pulling out from the matrix.

1. Introduction

Polyurea has been widely used in engineering waterproofing, anti-corrosion, vehicle wear resistance, equipment protection, and other fields, due to its durability, and resistance to corrosion, wear and impact. It is an elastomer material, with a strong buffer and energy absorption effect in engineering and equipment protection. However, its application is greatly limited due to its low crosslinking density, and its propensity to crack and fall off under conditions such as vibration and an alternating stress environment, [1–3]. In recent years, nanomaterials have been widely used in polymer matrix composites [4, 5]. Multiple studies have shown that nanocomposites formed by the addition of nanomaterials to polyurea, retain the advantageous properties of polyurea, and gain the mechanical properties and stability of nanomaterials. They have wide development and application potential in aerospace and automobile composite coatings and protection of equipment under alternating stress [6–8].

As an allotrope of carbon, carbon nanotubes (CNTs) have a one-dimensional hollow tubular structure, with a small radius. The outer diameter of the tube can range from a few, to tens of nanometers. The smaller inner diameter, can be as little as 1 nm. However, as its length is generally on the micron scale, its aspect ratio is very large. The carbon atoms of carbon nanotubes adopt sp² hybridization. At the same time, the hexagonal grid structure possesses a degree of flexibility and forms a spatial topological structure. This gives the carbon nanotubes extremely high modulus and strength [9]. In addition, the carbon-carbon bond has excellent stability,
which can effectively improve the tensile and tear strengths and stability of composites [10–12]. However, carbon nanotubes have a large surface area, due to their long tubular structure, so they easily become entangled and agglomerated by the action of internal Van der Waals forces. It is therefore difficult to achieve satisfactory dispersion in the polymer matrix [13, 14] using conventional mixing technology. Moreover, a weak interfacial bonding strength in the polymer matrix leads to poor wettability between the carbon nanotubes and the matrix [15, 16]. The large number of agglomerated CNTs in the matrix can also lead to stress concentration after curing, which further reduces the strength of the interfacial bonds. This seriously affects the load transfer between them and leads to the deterioration of some of the polymer matrix composites properties [8]. Investigation into how CNTs can be evenly distributed in the polymer matrix, and optimal performance achieved, is urgently needed [17].

The covalent and non-covalent functionalization of CNTs has greatly increased their application in polymer matrices. Covalent functionality involves introducing a polarization group at the CNTs end caps and side walls, by chemical reaction. The polarization group is then used as an intermediate site for further reactions to graft the chemical structure to the CNTs. Non-covalent functionality involves \( \pi-\pi \), hydrogen or electrostatic interactions being used to physically bind chemicals to carbon nanotubes. Both methods enhance the dispersion effect and wettability in the matrix. However, the application of non-covalent functionalization is limited due to the weak bond forces [18, 19]. Qian X et al [20] used amine-terminated polyether to treat graphene oxide. The functionalized graphene oxide (FGO) was then incorporated into a polyurea matrix using in situ polymerization. This resulted in a 60% increase in the tensile strength of the composites, with the addition of 0.5 wt% FGO, compared with original polyurea. Pingping A et al [21] used aminated CNTs as the reinforcing phase of polyurea composites. Their findings showed that when the content of aminated CNTs was 0.7 wt%, the dispersion in the polyurea matrix was relatively uniform. Composites with 0.7 wt% aminated CNTs showed the best mechanical properties, and tensile strength increased by 40%, compared with the original unmodified carbon nanotubes/polyurea composites. M T Müller et al [22] found that adsorption of polyoxyethylene cetyl ether on MWCNTs greatly reduces the percolation threshold of linear low-density polyethylene/multi-walled CNTs composites. Consequently, its elongation at break increased by 113% compared with composites without additives.

HDI trimer is triisocyanate, with an isocyanurate heterocyclic structure, with a higher molecular weight and functionality than monomer HDI. Moreover, one of the components used in the synthesis of polyaspartate polyurea (PAEP) is HDI trimer [23], which is highly compatible with PAEP matrix. Current research is limited to the functionalization of CNTs by isocyanate monomer [24, 25], but its application is also limited due to its high toxicity. Monomer HDI undergoes a trimerization reaction using a catalyst, and the resulting HDI trimer has low volatility, low toxicity, and good stability. It is therefore widely used as a curing agent for polyurethane and polyurea coatings [26]. However, research on the functionalization of CNTs with HDI trimer has not yet been published. In order to resolve the issue of CNTs aggregating in polymer matrix, and to improve the mechanical properties of polyaspartate polyurea (PAEP), HDI Trimer was used to covalently functionalize MWCNTs. This helps to overcome the adverse effects of van der Waals forces. The surface structure and chemical composition of CNTs before and after modification were characterized. The dispersibility, wettability and interfacial properties of HDI trimer functionalized MWCNTs (HDIT-MWCNTs) in PAEP were analyzed. The functionalized multi-walled carbon nanotubes reinforced polyurea composites (HDIT-MWCNTs/PAEP) were prepared, and their tensile properties and reinforcement mechanism were studied. These tests could be a base for the further use of HDIT-MWCNTs/PAEP composites.

2. Experimental

2.1. Materials

0.5–2 \( \mu \)m length and 20–30 nm diameter MWCNTs, with purity >95%, were purchased from Xianfeng Nanomaterials Technology Co., Ltd. (Jiangsu, China). HDI trimer was purchased from Yantai Wanhua Polyurethane Co., Ltd. (Shandong, China). Polyaspartate polyurea was purchased from Shandong Lianchuang Co., Ltd. (Shandong, China). It contains two components, in which component A is HDI trimer and component B is polyaspartate. N, N dimethylformamide (DMF) was purchased from Shandong Jiaying Chemical Co., Ltd. (Shandong, China). Dibutyltin dilaurate and ethyl acetate were purchased from Shanghai Jiuyi Chemical Reagent Co., Ltd. (Shanghai, China). Sulfuric acid, nitric acid, and deionized water were provided by Aladdin Reagent Co., Ltd. (Shanghai, China).

2.2. Synthesis of functional MWCNTs

Detailed steps in the preparation of functional MWCNTs:
1. Acidizing treatment of P-MWCNTs

200 mg of P-MWCNTs was added to a beaker filled with 240 mlH₂SO₄/HNO₃ (volume ratio 3:1) solution. The miscible liquid was vibrated ultrasonically for 2 h at room temperature; then heated to 60 °C and magnetically stirred for 5 h. After the reaction was complete, the solution was cooled to room temperature, and the centrifugation was carried out. The product was repeatedly washed with deionized water until the solution reached neutral pH, and then centrifuged. The resulting black solid was dried in a vacuum drying oven at 60 °C and ground to obtain carboxylated carbon nanotubes (COOH-MWCNTs) powder.

2. Grafting HDI trimer onto COOH-MWCNTs

10 g of HDI trimer was added (in excess) to 100 ml of DMF. A small amount of dibutyltin dilaurate was added to the solution as a catalyst. 150 mg of COOH-MWCNTs was then added. The solution was vibrated ultrasonically for 2 h at room temperature. When the reaction was complete, 150 ml of DMF was added. The solution was then filtered through a polytetrafluoroethylene membrane with a pore diameter of 0.45 microns. The residue was then repeatedly washed with ethyl acetate before additional filtration. The resulting solid was dried in a vacuum drying oven at 60 °C for 12 h. Finally, the black filter cake was ground to obtain HDI trimer grafted multi-walled carbon nanotubes (HDIT-MWCNTs).

2.3. Reaction mechanism of synthesis of functional MWCNTs

The functionalization reaction mechanism of HDI trimer modified multi-walled carbon nanotubes is shown in figure 1:

1. P-MWCNTs are long and intertwined. Firstly, the P-MWCNTs are destroyed and sheared by a H₂SO₄/HNO₃ solution. After treatment, the pipe length was shortened, and carboxyl groups were grafted onto the damaged area.

2. The structure of HDI trimer contains multiple isocyanate groups. Using a catalyst, isocyanate groups reacted with carboxyl groups on the end caps, or side walls, of CNTs to form amide groups. Some isocyanate groups did not react with the carboxyl groups and retained their original structure, thus forming HDI trimer modified carbon nanotubes (HDIT-MWCNTs).
2.4. Preparation of functional MWCNTs reinforced polyurea composites

Functional MWCNTs were added to component B (polyaspartate) of polyurea, and ultrasonically vibrated for 2 h. Then, component B and component A (HDI trimer) were mixed (volume ratio 1:2), and ultrasonically vibrated for 30 min. Subsequently, the solution was placed in a vacuum oven until no bubbles remained in the solution. The solution was poured into a polytetrafluoroethylene mold, coated with a release agent, and the functional MWCNTs reinforced polyurea composite was obtained after standing at room temperature for 14 days. The specific formulations are shown in Table 1.

3. Characterization and measurements

The structure of CNTs was characterized using a Fourier infrared spectrometer (Nicolett iS5). Samples were dried for 24 h before testing, and the scan resolution and scanning frequency were 4 cm$^{-1}$ and 32 times respectively. The scanning wavelength ranged from 4000 to 500 cm$^{-1}$.

TGA was performed using a TGA Q500 thermogravimetric analyzer (TA Instruments). Under nitrogen purging, a 5 mg sample was heated to 950 °C at a heating rate of 10 °C min$^{-1}$.

A contact angle measuring instrument (Shanghai Zhongchen JC2000DS) was used to measure the contact angle between CNTs and PAEP before and after modification.

The MWCNTs before and after modification were dissolved in DMF, and then dropped on the copper mesh after ultrasonic vibration. The dispersion state of carbon nanotubes before and after modification in organic solvent DMF, was studied by transmission electron microscope (Hitachi HT7800). MWCNTs/PAEP composites were prepared by adding 0.5 phr of CNTs before and after modification into a polyurea matrix. The composite material was cut into frozen 1 mm $\times$ 1 mm slices with a thickness of 50–60 nm. Then they were carried by copper mesh to observe the dispersion state of CNTs in the PAEP matrix before and after modification.

Tensile properties of MWCNTs/PAEP composites were measured according to ASTM D-638. Testing was performed using a CMT6503 microcomputer controlled electronic universal testing machine. The tensile speed of the sample was 200 mm min$^{-1}$, and the average value of five samples tested in each group was calculated.

Gold was sprayed on the cross section of the dumbbell-shaped sample after tensile fracture, and cross-section morphology was observed by scanning electron microscope (Hitachi S-4800).

4. Results and discussion

4.1. Characterization of functional carbon nanotubes

The FTIR of P-MWCNTs, COOH-MWCNTs and HDIT-MWCNTs is shown in Figure 2. The characteristic absorption peak of -OH appears at 3439 cm$^{-1}$ in P-MWCNTs, possibly due to the original CNTs containing a small amount of hydroxyl groups or the decomposition of crystal water during treatment. The characteristic absorption peak of -CH$_2$ appears at 2929 cm$^{-1}$. The characteristic absorption peak at 1624 cm$^{-1}$
is caused by the graphite structure in the CNTs skeleton. COOH-MWCNTs have a characteristic absorption peak of −OH at 3400 cm$^{-1}$. The characteristic absorption peak of −CH$_2$ appears at 2916 cm$^{-1}$. After mixed acid oxidation, the characteristic absorption peak of C=O in a carboxyl group appears at 1725 cm$^{-1}$. The characteristic vibration peak of C–H in-plane bending appears at 1393 cm$^{-1}$, and the stretching vibration peak of C–O single bond appears at 1170 cm$^{-1}$. The above results show that the P-MWCNTs were grafted with −COOH groups after acidification.

The FTIR of HDIT-MWCNTs shows the characteristic absorption peak of −OH at 3437 cm$^{-1}$, the stretching vibration peak of N–H at 3300 cm$^{-1}$, and the stretching vibration peaks of −CH$_2$ and −CH$_3$ at 2919 cm$^{-1}$ and 2854 cm$^{-1}$, respectively. The antisymmetric stretching vibration peak of C=N=O appears at 2275 cm$^{-1}$, indicating that isocyanate groups exist on the surface of HDIT-MWCNTs. The characteristic absorption peak of urea carbonyl C=O appears at 1630 cm$^{-1}$, the stretching vibration peak of C–N at 1545 cm$^{-1}$ and the characteristic absorption peak of C–N in isocyanurate ring at 1459 cm$^{-1}$. Based on the above results, HDI trimer has been successfully grafted onto the surface of carbon nanotubes.

Figure 3 shows the TGA curves of HDI trimer and MWCNTs. Figure 3(a) shows that HDI trimer begins to decompose at about 250 $^\circ$C, and the decomposition rate reaches 94.0% at 500 $^\circ$C. Figure 3(b) shows that the mass of the original carbon nanotubes is relatively unchanged when the temperature rises to 950 $^\circ$C, indicating that the P-MWCNTs have excellent thermal stability. After acidification, oxygen-containing groups, such as carboxyl groups, are grafted onto P-MWCNTs, which begin to decompose gradually at about 100 $^\circ$C. The decomposition rate of COOH-MWCNTs is about 8.19% at 950 $^\circ$C. HDIT-MWCNTs begin to decompose at 100 $^\circ$C due to the presence of oxygen-containing groups. The HDI trimer grafted onto the surface of MWCNTs decomposes violently at about 300 $^\circ$C, then stabilizes to a final decomposition rate of approximately 16.8%. The trend of the decomposition temperature and thermogravimetric curve of HDIT-MWCNTs is consistent with that of HDI trimer. This proves that HDI trimer is successfully grafted onto the surface of P-MWCNTs, and the grafting rate is 16.8%.

4.2. Wettability and interface properties of MWCNTs and PAEP
As a reinforcing phase, MWCNTs is added to the matrix material. It must be closely combined with the matrix material skeleton structure, so that the stress on the matrix can effectively be transferred and transmitted to MWCNTs. It is important to study the bonding force between MWCNTs and polyurea matrix skeleton structure for stress transfer and transmission in composites.

Excellent wettability between MWCNTs and polyurea matrix is helpful in improving the interfacial bonding strength. Wettability is achieved by measuring the contact angle of liquid on the surface. A large contact angle indicates that the surface is hydrophobic, whilst a small contact angle indicates a hydrophilic surface [28]. The wettability of MWCNTs in polyurea can be characterized by measuring the contact angle of PAEP matrix and MWCNTs. The results in figure 4 show that the contact angle of PAEP matrix and P-MWCNTs is 61.27$^\circ$. After acidification, the contact angle of PAEP matrix and COOH-MWCNTs is 41.21$^\circ$. After further modification, the contact angle of PAEP matrix and HDIT-MWCNTs is 32.92$^\circ$. The contact angle trend before and after modification is highly consistent with the conclusion given by Kwon, J. Y. [29]. The results show that the P-MWCNTs modified by HDI trimer, have excellent wettability in a polyurea matrix. According to the principle of similar compatibility, the modified CNTs have better wettability in the matrix.
The contact angle is determined by the surface free energy between solid and liquid, and the relationship between them is shown in formula (1). The adhesion work indicates the energy needed to separate the interface. In this paper, the Young-Dupre equation [30] is used to describe the relationship between surface free energy, adhesion work and contact angle (formula (2)).

\[ \gamma_s = \gamma_{SL} + \gamma_L \cos \theta \]  

(1)

\[ W_a = \gamma_s + \gamma_L - \gamma_{SL} = \gamma_L (1 + \cos \theta) \]  

(2)

In the formula, \( \gamma_s \), \( \gamma_L \), and \( \gamma_{SL} \) are the surface free energy of solid, liquid and solid-liquid, respectively. \( W_a \) is the adhesion work of the solid-liquid interface, and \( \theta \) is the contact angle.

In this paper, the surface free energy of solid and liquid are calculated according to the Owens and Wendt surface energy component method [31]. The solid-liquid interface interaction can be expressed as:

\[ \gamma_{SL} = \gamma_s + \gamma_L - 2\sqrt{\gamma_s \gamma_L} - 2\sqrt{\gamma_s^{d} \gamma_L^{d}} \]  

(3)

In the formula, \( \gamma_s^{p} \) and \( \gamma_s^{d} \) are polar components of surface free energy of solid and liquid, and \( \gamma_L^{d} \) and \( \gamma_s^{d} \) are dispersive components of surface free energy of solid and liquid. In which:

\[ \gamma_s = \gamma_s^{p} + \gamma_s^{d} \gamma_L = \gamma_L^{p} + \gamma_L^{d} \]  

(4)

The above formulas can be obtained simultaneously:

\[ \gamma_L (1 + \cos \theta) = 2\sqrt{\gamma_s \gamma_L^{p}} + 2\sqrt{\gamma_s^{d} \gamma_L^{d}} \]  

(5)

In this paper, water and diiodomethane with different surface free energy components are used to determine the surface free energy of MWCNTs solids. It is known that the surface free energy of polyurea is 51.9 mJ m\(^{-2}\) [32]. The \( \gamma_s^{p} \) and \( \gamma_s^{d} \) of water are 51 and 21.8 mJ m\(^{-2}\), and the \( \gamma_L^{d} \) and \( \gamma_s^{d} \) of diiodomethane are 0 and 50.8 mJ m\(^{-2}\) respectively [33]. The results in table 2 show the surface free energy of HDIT-MWCNTs is 68.71 mJ m\(^{-2}\), which is 63.3% higher than that of P-MWCNTs (42.09 mJ m\(^{-2}\)). These surface free energy values are highly consistent with the conclusions of Zhang, R. L. [34]. The results can mainly be explained by the increase in MWCNTs surface polarity weight after modification. The magnitude of the polarity component is affected by surface polarity factors, including the interaction between dipole and hydrogen bond [35]. The amide bond and isocyanurate ring in HDIT-MWCNTs structure can enhance the interaction between dipole and hydrogen bond, so that the surface free energy of HDIT-MWCNTs is greatly increased compared to before modification.

Table 2. Contact angles of water and diiodomethane with MWCNTs and surface energy of MWCNTs.

| Contact angle(°) | Surface energy(mJ m\(^{-2}\)) |
|-----------------|-------------------------------|
|                 | Water | Diiodomethane | \( \gamma_s^{p} \) | \( \gamma_s^{d} \) | \( \gamma_L \) |
| P-MWCNTs        | 95.9  | 35.1          | 0.11            | 41.98 | 42.09 |
| COOH-MWCNTs     | 58.5  | 14.8          | 10.10           | 49.12 | 59.22 |
| HDIT-MWCNTs     | 40.7  | 11.3          | 18.89           | 49.82 | 68.71 |

Table 3. Adhesion work and interfacial energy of PAEP and MWCNTs.

|                   | Adhesion work(mJ m\(^{-2}\)) | Interfacial energy(mJ m\(^{-2}\)) |
|-------------------|-------------------------------|----------------------------------|
| P-MWCNTs          | 76.85                         | 17.14                            |
| COOH-MWCNTs       | 90.94                         | 20.17                            |
| HDIT-MWCNTs       | 95.47                         | 25.14                            |

Figure 4. Contact angles between MWCNTs and PAEP. (a) P-MWCNTs and PAEP (b) COOH-MWCNTs and PAEP (c) HDIT-MWCNTs and PAEP.
By inputting the surface free energy data of MWCNTs solid into formulas (1) and (2), the solid-liquid interface free energy of MWCNTs solid and PAEP matrix was calculated. Table 3 shows that the surface free energy and adhesion work of P-MWCNTs are 17.14 mJ m\(^{-2}\) and 76.85 mJ m\(^{-2}\), respectively. The surface free energy and adhesion work of modified HDIT-MWCNTs are 25.14 mJ m\(^{-2}\) and 95.47 mJ m\(^{-2}\); increases of 46.7% and 24.2% compared with P-MWCNTs, respectively. The results show that the interfacial free energy between MWCNTs and polyurea matrix after surface functionalization is the highest, the energy required for separation is greatly increased, and the interfacial adhesion is the strongest.

### 4.3. Dispersion of Functional MWCNTs in DMF and PAEP

A thorough dispersion of MWCNTs in the organic solvent (DMF) is crucial for uniform distribution in the PAEP matrix. Figure 5 shows the TEM diagram of dispersion state of P-MWCNTs, COOH-MWCNTs and HDIT-MWCNTs in DMF. In the figure 5, several untreated P-MWCNTs are gathered and entangled together. After mixed acid oxidation, the end of the MWCNTs was opened, and the carboxyl was grafted onto the end cap and side wall. This improved the dispersion performance of MWCNTs in DMF. After modified by HDI trimer, MWCNTs are uniformly dispersed in DMF without obvious agglomeration. This is because dispersion and the interface performance of HDIT-MWCNTs in DMF are greatly improved after modification [36].

To further investigate the dispersion effect of MWCNTs in the PAEP, the frozen ultra-thin slices of MWCNTs/PAEP composites were observed, and the TEM are shown in figure 6. It is evident that P-MWCNTs have serious agglomeration phenomenon, and the dispersion performance of COOH-MWCNTs in polyurea matrix has been improved. HDIT-MWCNTs has the best dispersion effect in polyurea matrix without obvious agglomeration phenomenon. The results prove that the functional methods adopted in this paper can effectively upgrade the dispersion performance of MWCNTs in PAEP.

### 4.4. Tensile properties of MWCNTs reinforced polyurea composites

The tensile stress-strain curves, tensile strength and Young’s modulus of PAEP and MWCNTs/PAEP are shown in figure 7 and 8. The composites tensile results are consistent with those of Tian, J [13] and Qi, Z [37]. Namely, that the composites fracture characteristics did not change when P-MWCNTs and HDIT-MWCNTs were added into PAEP matrix. However, the slope, and extreme value of stress-strain curves are different. Figure 8(a) shows when P-MWCNTs was added to the matrix, its tensile strength decreased as the amount added increased. This is because P-MWCNTs have poor dispersion in the matrix due to the strong van der Waals forces, leading to the
phenomenon of stress concentration, and a subsequent decrease in tensile strength. Adding 0.5 phr HDIT-MWCNTs increases the tensile strength of the composite from 13.85 MPa to 17.78 MPa, which is 28.4% higher than that of the original matrix. This is because the surface of MWCNTs modified by HDI trimer, is grafted with amide bond and an isocyanurate ring. This rigid structure increases the degree of hydrogen bonding, the density of crosslinking points, the intermolecular force and steric effects, thus improving tensile strength. This conclusion concurs with research by Zhang, J [38] and X, Lu [39]. We can conclude that the improvement in the composites’ tensile properties is attributed to the increase of hard segments in the composites.

Figure 8(b) shows that the Young’s modulus of the composites material decreases initially, before increasing and decreasing again. The Young’s modulus reaches its maximum of 170.31 MPa when the addition amount is 0.5 phr HDIT-MWCNTs. This is 90.84% higher than that of the original matrix of 89.24 MPa. This is because when HDIT-MWCNTs are added to the matrix, they occupy the spaces between the molecular chains of the matrix, thus limiting the movement of the soft and hard molecular chains. When the composites are under stress, the stress borne by HDIT-MWCNTs increases while the restriction on the movement of the molecular chain increases, resulting in the increase in Young’s modulus [40].

4.5. Study of tensile section morphology and strengthening mechanism of PAEP and MWCNTs/PAEP composites

Material fracture usually at the weakest points within it. Cracks propagate through one or more points, generating new cracks, until finally the material breaks after reaching its critical stress point. Figure 9 shows the
tensile cross-sectional morphology of PAEP, P-MWCNTs/PAEP and HDIT-MWCNTs/PAEP composites. In figure 9(a), the cross section of pure PAEP is mostly river-like or radial (marked by the white circle). From the high-power SEM picture in figure 9(b), we can observe the regular strip, or step-like morphology (indicated by the white arrow), when the crack propagates, demonstrating that the crack propagates freely without hindrance. This indicates that the mechanical properties of pure PAEP are poor [41].

In figure 10, the cross section of P-MWCNTs/PAEP composites retains the typical river-like (marked by the white circle) and step-like morphology (indicated by the white arrow) of partially pure PAEP. However, due to a large amount of agglomeration of P-MWCNTs, the interfacial bonding strength between P-MWCNTs and the substrate is extremely low. This leads to micropores and gaps around P-MWCNTs, hence the material breaks at the defects and forms an irregular tear-like morphology (marked by the red circle). The tensile properties of P-MWCNTs/PAEP are noticeably lower than those of pure PAEP.

It can be seen from figure 11 that the tensile section of HDIT-MWCNTs/PAEP composites is coarser than that of pure PAEP. The deflection and bifurcation of cracks (indicated by the red arrow) can be clearly seen. The typical regular river shape morphology of pure PAEP (shown by the white circles) and step shape (indicated by the white arrow) can be retained at the same time. Since the crack can only propagate in the near interface area between HDIT-MWCNTs and the substrate, when the crack is hindered during the propagation process, it may change direction and deflect. Some cracks produce obvious bifurcation phenomenon, which can dissipate more energy. The multiple dimples that appeared are marked by the white box. This is because HDIT-MWCNTs hindered the crack propagation, while some HDIT-MWCNTs were pulled out of the matrix. After surface functionalization, MWCNTs have strong wettability with the PAEP matrix. In the process of pulling out, the matrix is plastically deformed, and is attached to the surface of HDIT-MWCNTs, therefore dimple-like pits are formed. Consequently, the composites modified by HDIT-MWCNTs have the best tensile properties. This conclusion agrees with that of Qiao, J et al [42].
5. Conclusion

(1) After P-MWCNTs were oxidized by sulfuric acid and nitric acid, carboxyl groups were introduced onto its surface. HDI trimer was successfully grafted onto the MWCNTs surface by the reaction between carboxyl groups and isocyanate groups on HDI trimer.

(2) After surface functionalization modification, the dispersion, wettability and interface properties of HDIT-MWCNTs and PAEP matrix were greatly improved. The contact angle of PAEP and HDIT-MWCNTs is 32.92°, which is about 46.3% lower than that between P-MWCNTs and PAEP (61.27°). The surface free energy of HDIT-MWCNTs is 68.71 mJ m⁻², an increase of 63.3% compared with 42.09 mJ m⁻² of P-MWCNTs. The interfacial energy and adhesion work between PAEP and HDIT-MWCNTs are 25.14 mJ m⁻² and 95.47 mJ m⁻², respectively. These figures are 46.7% and 24.2% higher than those of P-MWCNTs and PAEP (17.14 mJ m⁻² and 76.85 mJ m⁻², respectively).

(3) The tensile properties of functionalized HDIT-MWCNTs reinforced polyurea composites (HDIT-MWCNTs/PAEP) were significantly improved. When 0.5 phr HDIT-MWCNTs was added, the maximum composite tensile strength reached 17.78 MPa, which is 28.4% higher than that of the pure PAEP of 13.85 MPa. The Young’s modulus reached 170.31 MPa, which is 90.84% higher than that of the pure PAEP of 89.24 MPa.

(4) The deflection and bifurcation of cracks were observed in the tensile section of HDIT-MWCNTs/PAEP, and dimple-like pits appeared. This is because HDIT-MWCNTs hinders the propagation of cracks and that some HDIT-MWCNTs were pulled out from the PAEP matrix. The interfacial bonding strength between HDIT-MWCNTs, after surface functionalization, and PAEP matrix is greatly improved. There is PAEP matrix adhesion on HDIT-MWCNTs when pulled out, resulting in plastic deformation of the matrix. In both cases, more energy can be dissipated to improve the mechanical properties of the composites. Therefore, the strengthening mechanism of HDIT-MWCNTs on PAEP is mainly manifested by the deflection and bifurcation of cracks caused by HDIT-MWCNTs, and the plastic deformation of PAEP matrix caused by HDIT-MWCNTs pulling out from the matrix.
Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

Author contributions

Investigation, H W; Project administration, Z Z; Supervision, J T; Writing—original draft, X L; Writing—review & editing, Y T.

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Conflicts of interest

The authors declare no conflict of interest.

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