Preparation and Properties of Polyurethane Nano - inorganic Composite Environmentally Friendly Building Materials

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Waterborne polyurethane is a polyurethane binary collagen system with water as the dispersion medium. It has the advantages of environmental protection, strong adhesion, high hardness, good flexibility, good air permeability and non-flammable. Therefore, waterborne polyurethanes can be used in the fields of coatings, leather, ink, textile, adhesives and building materials. In addition, it can also be used for special functional materials. However, compared with solvent-based polyurethane, water-based polyurethane has many shortcomings, such as water resistance, mechanical properties and heat resistance are not very good. Therefore, in order to improve the overall performance of waterborne polyurethane, we synthesized new water-based polyurethane.

1. Introduction

Polymeric compounds of many repeating polyurethanes (-NH-COO-) are known as polyurethanes (PU). Polyurethane structure contains mainly urethane bond, urea bond and ester groups, so the polyurethane coating has excellent flexibility, abrasion resistance, strong adhesion, low temperature resistance and chemical resistance (Hölken et al., 2016; Zhao and Yuan, 2016; Rusman et al., 2017; Gabriel et al., 2016). Because of these characteristics, it is widely used as paint, ink, elastomer, adhesives, leather and sealing materials (Zhang et al., 2017).

HNTs nanotubes are a kind of low cost natural nanotubes with double layer 1:1 type aluminum silicate. Its molecular formula is $Al_2Si_2O_5(OH)_4$ $nH_2O(n=0$ or 2). It has a typical crystalline structure, which consists of the inner layer of aluminum oxide octahedron and the outer layer of silicon tetrahedral lattice. There is crystal water between layers (Pielichowska et al., 2014). It was found that HNTs contains two kinds of silicon hydroxyl groups that located on the outer surface of HNTs and more aluminum hydroxyl groups that located between the layers. HNTs are added to the polymer to produce nanocomposites, which can greatly improve the mechanical properties, thermal stability and flame retardancy of the polymer (Zhang, et al., 2017; Li et al., 2016; Li et al., 2017). However, the HNTs particles are subjected to hydrogen bonding between the surface hydroxyl groups and the size effect, which is easy to agglomerate in the matrix, resulting in unsatisfactory dispersion effect, thus affecting the application effect. Therefore, it is necessary to modify the HNTs particles before use (Milián, et al., 2017). The common modification methods are coupling agent modification, surface coating modification, intercalation modification and free radical modification (Yang et al., 2015).

Silane coupling agent modification is the most commonly used method for HNTs modification. The principle is to use the silane coupling agent after the hydrolysis of amphiphilic to enhance the dispersion of HNTs and interface compatibility (Saba, et al., 2014). Zhao Chao (2013) use the KH570 silane coupling agent to treat HNTs particles, and the results of thermogravimetric analysis (TG) were 1.06 mmol/g. Liu Mingxian (2015) modified HNTs with 3-glycidyl ether propyl trimethoxysilane and compounded it with epoxy resin. As a result, the thermal decomposition residual carbon ratio, bending performance and storage modulus of the composites are effectively improved. The intercalation modification is based on the use of small organic molecules containing hydroxyl or amino groups in the HNTs coil forming layer, which makes it better dispersed in the resin matrix (Wan et al., 2015). The HNTs were intercalated with phenylphosphoric acid (PPA), which

changed it from nanotubes to nanocomposites, increasing their contact area with the matrix and improving the interface compatibility (Saba, et al., 2016).

2. Experimental part

2.1 The main raw materials and laboratory equipment

Table 1: The materials of experiment

Name	Specification	Manufacturer
HNTs nanotubes	Industrial grade	Origin: Hubei Yichang
Polyethylene glycol 1000	Industrial grade	Yantai Huada Chemical Co., Ltd
KH-500	Pure chemical	Tianjin Kewei Chemical Co., Ltd
Anhydrous ethanol	Pure chemical	Tianjin Kewei Chemical Co., Ltd
Leveling agent	Pure chemical	Bayer
Waterborne dispersant	Pure chemical	Bayer

Table 2: The equipment of experiment

Equipment name	Model	Manufacturer
Fourier infrared spectrometer	8400s	Japan Shimazdzu company
Electric heating oven	DH-101-BS	Tianjin Central Experimental Electric Furnace Co., Ltd
Constant temperature magnetic stirrer	EMS-8C	Tianjin Ounuo Instrument Co., Ltd.
Scanning electron microscope	S-4800	Japan Hatchi company
Recycling multi - purpose vacuum pump	SHB	Zhengzhou Great Wall Branch Industry and Trade Co., Ltd
Universal testing machine	M350-20KN	Shenzhen SANS Testing Machine Co., Ltd
X - ray diffractometer	D/max 2500v/pcX	Japan Rigaku
Differential thermal scanning calorimeter	DSC 200 F3	Germany Netzsch Co., Ltd

2.2 Different methods of modifying HNTs

2.1.1. Purification of HNTs particles
A certain amount of HNTs particles are added to 100 mL of absolute ethanol, stirred for 1 h, and then subjected to ultrasonic dispersion for 30 min until a homogeneous suspension is formed. The prepared suspension is filtered and the supernatant powder is dried in an oven at 60 °C until no change in mass is obtained. Then, HNTs particles without impurities are sieved.

2.2.2. Modification of HNTs
(1) KH550 organic modification
6.0 g of purified HNTs are added to a mixed solution of 90 mL of ethanol and 10 mL of deionized water. Ultrasound is used to form a homogeneous suspension. 1.5g of the aminosilane coupling agent KH550 is added dropwise to the suspension for 12 hours while stirring, and the resulting powder is allowed to react in an oven at 120C for 2 hours. The active amino group powder is ground into powder by coupling reaction and sieved with 200 mesh sieves to obtain organic HNTs particles, which are designated as K-HNTs.
(2) PEG organic intercalation
6.0 g of purified HNTs are added to 100 mL of deionized water and dispersed using ultrasound to form a homogeneous suspension. 30g polyethylene glycol is added to the suspension, and the temperature is raised to 60 °C. After stirring for 4 hours, the mixture is filtered. The resulting powder is dried in an oven at 60 °C without any change in mass. The powder is ground into powder and sieved with a 200 mesh sieve to obtain intercalated HNTs particles, designated P-HNTs.
(3) Rare earth modification
The Ce(NO3)3·6H2O is partitioned into an aqueous solution with a mass concentration of 1.2 wt%. 6.0 g of purified HNT is added to 100 mL of the well-prepared rare earth solution. Ultrasound is used to form a homogeneous suspension. The suspension is allowed to stand for 5 h at room temperature and then filtered. The resulting powder is dried in an oven at 60 °C without any change in mass. The powder is ground into powder and sieved with a 200 mesh sieve to obtain rare earth modified HNTs particles, designated Ce-HNTs.

2.2.3. Preparation of WPU / HNTs composites

A 100 g aqueous polyurethane emulsion is prepared with a solid content of 35 and weighed 0.35 g (corresponding to 1% by volume of the system). The K-HNTs particles prepared in the above procedure are added to the WPU emulsion. Appropriate amount of aqueous dispersant and leveling agent is added. At high shear, it is mixed. The emulsion is poured into a self-made polytetrafluoroethylene mold, dried at room temperature and then dried in an oven at 60 °C until no change in quality. According to this procedure, the water-based polyurethane composite film with K-HNTs mass fraction of 2%, 3%, 4% and 5% is prepared. According to the above steps, an aqueous polyurethane composite film containing P-HNTs particles and Ce-HNTs particles with a mass fraction of 1%, 2%, 3%, 4% and 5% is prepared.

2.2. 4. Analysis and test

(1) Analysis of infrared spectrum

The groups of the product are characterized by FT-IR 8400s infrared spectroscopy (FT-IR). The samples are mixed with potassium bromide (KBr) before the test, and the tablets are milled and scanned for a range of 500 to 4000 cm^{-1}.

(2) Performance test of mechanical property

The tensile strength and elongation is carried out in Shenzhen SANS M350-20KN universal material testing machine. The test standard is GB/T1040-1992. The initial measurement length is 20mm, the test environment is room temperature 25 °C, and the tensile speed is 50mm / min. Each sample should be tested at least five. The error should be controlled within 5%. At last, the mean value is calculated.

(3) Analysis of differential scanning calorimetry

Differential scanning calorimetry is performed on the German NetzschDSC200F3 tester. Under high purity nitrogen protection, the nitrogen flow rate is 30 ml / min and the sample weight is 2~3 mg. The temperature is loared to -50 °C at a cooling rate of 10 °C / min and the temperature is raised to 200 °C at 10 °C / min, and the crystallization curve of DSC is recorded.

3. Results and discussion

3.1 FTIR analysis of modified HNTs with different methods

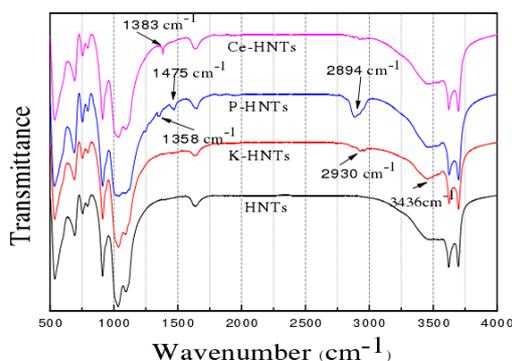The infrared spectra of HNTs and modified HNTs are shown in Figure 1.

Figure 1: The FR-IR image of the HNTs and modified HNTs

It can be seen from Figure 1 that the peak near 3700-3600 cm^{-1} is the characteristic peak of HNTs. Among them, in the vicinity of 3696cm^{-1}, it is a layered structure formed of silicon oxygen tetrahedron and alumina eight surface body surface non-shared -OH absorption peak. In the vicinity of 3620cm^{-1}, it is a layered structure of silicon oxygen tetrahedron and alumina eight surface constitute the internal surface sharing -OH absorption peak. In the vicinity of 1028cm^{-1}, it is the stretching vibration absorption peak of the Si-O-Si bond. In the vicinity of 910cm^{-1}, it is the bending vibration peak of Al-OH bond. The stretching vibration peak of 2930cm^{-1}-C-H, the NH stretching vibration peak of 3436cm^{-1} and the stretching vibration peak of Si-O at 1100cm^{-1} were appeared in the infrared spectrum of HNTs after KH550 modification, which shows that KH550 is well coupled to HNTs. The absorption peak near 2894 cm^{-1} and the double absorption peak near 1358 cm^{-1}, 1475 cm^{-1} were added to the infrared spectrum of HNTs after PEG-PEG, which was the characteristic peak of the -CH2 group in PEG structure, indicating that PEG was well intercalated for HNTs.

3.2 Analysis of mechanical properties of different materials

Figure 2 is a comparison of the tensile strength of the modified HNTs-WPU composites and the HNTs-WPU composites modified by different methods.
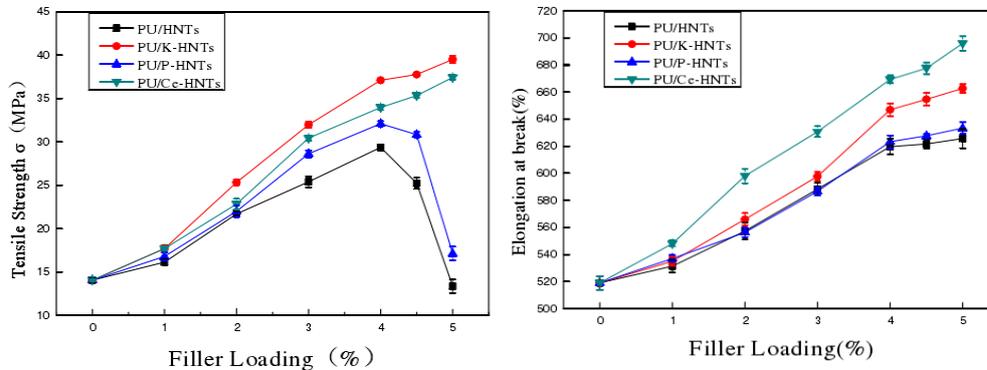

Figure 2: The tensile strength and elongation at break of WPU/HNTs with different modified methods

As can be seen from Figure 2, in the waterborne polyurethane system with unmodified HNTs, the tensile strength was increased first and the maximum value was 27.5Mpa at about 4%, and the strength was about 1.7 times of the blank WPU with the increase of HNTs content. As the HNTs content continues to increase, the tensile strength of the composites was decreased. The reason is that HNTs is a kind of inorganic material, it has certain strength. When added to the organic matrix, it can improve the WPU hard segment content, and the strength of the material is improved. In addition, HNTs is a rod like structure, which is easier to disperse and disperse than spherical particles under the same processing conditions.

3.3 Analysis of differential scanning calorimetry

Figure 3 shows the DSC curves for the WPU and the composites of the WPU and several modified HNTs particles.
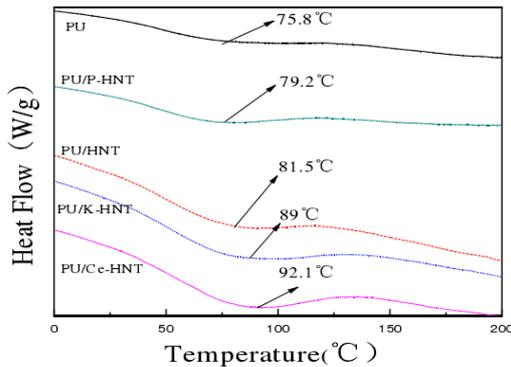

Figure 3: The DSC image of different WPU/HNTs

It can be seen from Figure 3 that the glass transition phenomenon of pure WPU is not obvious. With the addition of HNTs particles, the glass transition temperature of the soft segment molecular chains of WPU composites was improved obviously. The reason is that the HNT particles are dispersed in the polyurethane matrix and embedded in the polyurethane matrix as the hard segment of the polyurethane, which is equivalent to the increase of the hard segment in the polyurethane matrix, so as to lead to the glass transition temperature of the soft segment of the polyurethane matrix was increased from 75.8 °C to 81.5 °C. The glass transition temperature of the composites was improved obviously after the rare earth modified composites. Because the rare earth elements form a covalent bond with the polyurethane backbone, the bond and bond strength is stronger than that of the hydrogen bond, which makes the segment movement of the soft segment in the polyurethane matrix be restricted, so the glass transition temperature of the soft segment is obvious.

3.4 Analysis of mechanical properties of different materials

Figure 4 shows the relationship between the water absorption and the time of WPU composite film with different content of HNTs inorganic nanotubes. Figure 5 shows the relationship between the water absorption and the time of the WPU composite film modified by the HNTs nanotubes with different methods.
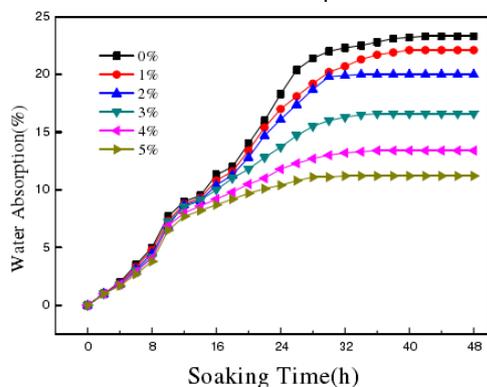

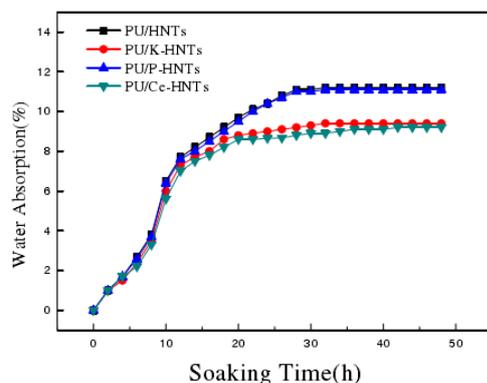*Figure 4: The relation of water absorption of WPU/HNT with different HNTs contents*

Figure 5: The relation of water absorption of WPU/modified-HNT with different HNTs contents

As can be seen from Figure 4, although the surface of the HNTs and the surface of the wall is hydrophilic particles, the surface hydroxyl density is small, so the addition of polyurethane matrix does not significantly increase its hydrophilicity. On the contrary, with the increase of HNTs content, the water resistance of the film was gradually improved. The reason is that HNTs are rigid inorganic particles, which can increase the water-based polyurethane hard segment micro-area. The hard segment that acts as a waterborne polyurethane causes crosslinking within the resin. As the degree of crosslinking increases, the hardness and strength of the film are increased. The difficulty of water entering into the resin is increased, which leads to the low water absorption rate and good water resistance.

As can be seen from Figure 5, after KH550 and rare earth modification, HNTs can significantly improve the water resistance of the resin. The reason is that the surface of the HNTs modified by KH550 has a hydrophobic group, which can reduce the number of hydroxyl groups on the surface and the wall of the HNTs and thus evenly disperse in the matrix. However, the water resistance of rare earth modified was improved significantly. The reason is that rare earth elements and resin backbone and HNTs surface hydroxyl groups can form a coordination bond, which can improve its interface compatibility. The dense network structure is formed to reduce the probability of water molecules entering, and the water absorption of the polyurethane film becomes low. PEG-modified HNTs did not significantly improve the water resistance of the films. The reason is that PEG contains hydroxyl, and its intercalation increases the density of OH in the tube wall of HNTs. However, the intercalation is unstable, the hydrophilicity of HNTs is not significantly changed, so that the water resistance of the composites is not affected.

4. Conclusions

(1) The analysis of FT-IR data confirms that PEG, KH550 and strontium nitrate have successfully modified HNTs. Among them, PEG belongs to the intercalation modification, KH550 belongs to the modification of coupling agent, and the rare earth compound belongs to the modification of surface coordination bond.

(2) The mechanical properties of WPU / HNTs composites have been improved by DSC and mechanical properties. The modified HNTs can further improve the tensile strength of the composites. The elongation at break of composites increases with the increase of HNTs content, which indicates that HNTs can enhance and improve the performance of waterborne polyurethane at the same time.

(3) The results show that the modified particles can effectively increase the initial decomposition temperature and glass transition temperature by DSC test. The water resistance test shows that the water resistance of WPU/HNTs composites has been improved obviously. With the increase of HNTs content, the water absorption of the composites decreased and the water resistance became better. It is concluded that the inorganic nanotubes containing hydroxyl groups play an important role in the modification of waterborne polyurethane.

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