



# Reinforcing thermoplastics with hydrogen bonding bridged inorganics

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## ABSTRACT

A new reinforcing strategy for thermoplastics via hydrogen bonding bridged inorganics in the matrix was proposed. The hydrogen bonds could be formed in thermoplastics matrices with the incorporation of a little organics containing hydrogen bonding functionalities. Isotactic polypropylene (PP), polyamide 6 (PA 6), and high density polyethylene (HDPE), together with specific inorganics and organics were utilized to verify the effectiveness of the strategy. The investigations suggest that the hydrogen bonding bridged inorganics led to substantially increased flexural properties. The results of attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) and X-ray photoelectron spectra (XPS) indicate the formation of hydrogen bonding among the inorganics and organics in the composites.

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## 1. Introduction

So far, polymer materials have become one of the most important materials and have been widely used in numerous applications. However, compared with metals and ceramics, the mechanical properties of polymer materials, especially thermoplastics, are far from satisfied. As a consequence, the reinforcement of thermoplastics has always been the highlight in polymer material area [1–3].

At present, many strategies have been proposed for reinforcement purpose, mainly including compounding with inorganics, chemical modifications such as crosslinking, and formation fiber reinforced composites [4–6]. Among them, incorporation of inorganics is one of the most convenient and favored strategy for their advantages such as easily scale-up, cost competitive and unsophisticated. However, the low compatibility between inorganics and most of thermoplastics is always the hindrance which restricting the further application of the strategy [7,8].

Traditionally, the interface and compatibility are the crucial factors for the mechanical properties of plastics/inorganic filler composites. Recently, a new strategy was proposed irrespective of the low compatibility between inorganics and thermoplastics [9]. This is achieved by the hydrogen bonding bridged inorganics in polymer matrix during processing between the inorganics and the organic molecules which are capable of donating or accepting protons. This strategy is suitable for low polarity plastics such as

polyolefins and also applicable to polar plastics such as polyamides. Compared with the conventional method such as utilizing coupling agents to improve the compatibility of the plastics/inorganic filler composites, the present method exhibits much effective reinforcing effects and the process is much facile.

The present work intends to further verify the effectiveness of the strategy in reinforcing different thermoplastics through hydrogen bonding bridged inorganics during processing. A number of organics were incorporated to form hydrogen bonds with inorganics. The effectiveness of this strategy to isotactic PP, HDPE and PA 6 were examined.

## 2. Experimental

### 2.1. Materials

Isotactic PP granules, with a melt flow index of 2.84 g/10 min (after ISO-1133: 1997(E)), were obtained from Guangzhou Petrochemical Co. Ltd.

HDPE powder was supplied by Guangzhou Petrochemical Co. Ltd. with a melt flow index of about 10.0 g/10 min.

PA 6 chips, with trademark of ZISAMIDE, were purchased from Zig Sheng Industrial Co., Ltd. The melt flow index was determined as 45 g/10 min.

The halloysite nanotubes (HNTs) were collected from Hubei Province, China. The HNTs were purified via repeated washing/centrifugation process. The Brunauer-Emmett-Teller (BET) surface area was determined as 50.45 m<sup>2</sup>/g.

Precipitated silica was gifted by Zhuzhou Xinglong Chemical Enterprise Co. Ltd, China, with BET surface area of 166.49 m<sup>2</sup>/g.

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Calcium carbonate was analytic grade reagent manufactured by Tianjin Kermel Chemical Reagents Development Center.

All the organics, melamine (MEL), melamine cyanuric acid (MCA), diphenyl guanidine (DPG), 2,4,6-trimercapto-s-triazine (TCY), tri-(2-hydroxyethyl) isocyanurate (THEIC), beta-cyclodextrin (beta-CD) are commercial available and used as received.

## 2.2. Preparation of thermoplastics composites reinforced by inorganics

The thermoplastics composites were prepared with a twin-screw extruder. For isotactic PP, PA 6, and HDPE systems, the temperatures setting from the hopper to the die were 180/200/200/200/200 °C, 220/240/240/240/240 °C and 180/200/200/200/200 °C respectively. The screw speed was 100 rpm, and the pelletized granules of PP, PA 6 and HDPE were dried for 5 h under 80, 120 and 80 °C respectively. Then granules were injection molded to the specimens for mechanical determinations at 200, 240 and 200 °C respectively.

## 2.3. Characterizations

**Mechanical properties determinations:** Shimadzu AG-1, Instron 4465 and Zwick pendulum 5113.300 were used to perform the tensile, flexural and impact testing according to ISO 527: 1993, ISO 178: 1993 and ISO 180: 1993 respectively.

**Dynamic rheological measurements:** Dynamic rheological behavior measurements of the PP composites were performed on a RDA III dynamic rheometer in oscillatory shear using a parallel plate system with the diameter of 25 mm. The gap of the plate was set as 1.5 mm. The strain range was set as 0.01–300%. The measurements were performed at 200 °C and the frequency was set as 10 rad/s.

**Fourier transform infrared spectroscopy (FTIR):** HNTs, precipitated silica and calcium carbonate powders were sheet molded with potassium bromide respectively. The FTIR analysis was conducted by a Bruker Vector 33 spectrometer. Spectra were taken from 4000 to 400  $\text{cm}^{-1}$  wavenumbers.

**Attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR):** HNTs powder, the organics and the model mixtures of HNTs and the organics were sheet molded to small discs (about 2 mm thick and diameter about 10 mm) at pressure of about 8.0 MPa. Then the little discs were analyzed by a Bruker Vector 33 spectrometer. Thirty-two consecutive scans were taken at each sampling time, and their average was stored. Spectra were taken from 4000 to 400  $\text{cm}^{-1}$  wavenumbers.

**X-ray photoelectron spectra:** X-ray photoelectron spectra of MEL and PP/HNTs/MEL composite were recorded by using an X-ray photoelectron spectrometer (Kratos Axis Ultra DLD) with an Aluminum (mono)  $K_{\alpha}$  source (1486.6 eV). The Aluminum  $K_{\alpha}$  source was operated at 15 kV and 10 mA. For all the samples, a low-resolution survey run (0–1100 eV, pass energy=160 eV) was performed. In order to obtain more information about the formation of hydrogen bonding, a high-resolution survey (pass energy=48 eV) was performed at spectral regions relating to nitrogen.

**Scanning electron microscopy (SEM):** The fracture surface of impact samples were plated with a thin layer of gold before the observations. The SEM observations were then done using LEO1530 VP SEM machine.

**Transmission electron microscopy (TEM):** The specimens were ultramicrotomed into thin pieces of about 120 nm in thickness with Leica EM UC6. Then the TEM observations were done using a Philip CM12 electron transmission microscope machine at an accelerating voltage of 30 kV.

**Differential scanning calorimetry (DSC):** DSC data was measured by NETZSCH DSC204 F1 using nitrogen as purging gas. The PP composites were heated to 200 °C at ramping rate of 20 °C/min. The sample was kept at 200 °C for 5 min to eliminate the thermal history before it was cooled down to 40 °C at rate of 10 °C/min. After kept at 40 °C for 3 min, the sample was reheated to 200 °C at ramping rate of 10 °C/min. For the PA 6 composites, all the samples were heated to 260 °C and cooled down to 120 °C at rate of 10 °C/min. The exothermic flows were recorded as a function of temperature.

## 3. Results and discussion

### 3.1. Reinforcing effects of the hydrogen bonding bridged inorganics to thermoplastics

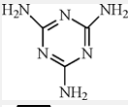
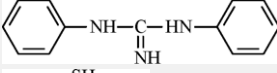
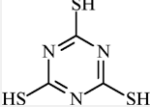
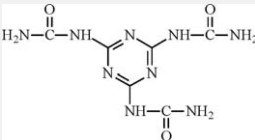
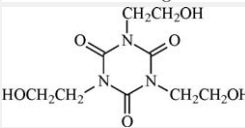
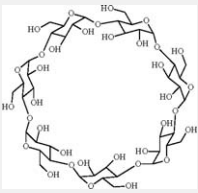
Generally, the polarity discrepancy between the thermoplastics and the inorganics determines their compatibility and the compatibility have tremendous effects on the mechanical properties of inorganics filled thermoplastics composites. Consequently the interfacial interactions between inorganics and thermoplastics are always the highlight for thermoplastics composites. Currently, a new reinforcing strategy for thermoplastics via hydrogen bonding bridged inorganics was proposed, and the present strategy for reinforcing thermoplastics are irrespective the compatibility between matrix and inorganics. In the investigation, two typical types of non-polar thermoplastics, isotactic PP and HDPE, and a typical type of polar thermoplastics, PA 6, were utilized to verify the effectiveness of the reinforcement strategy. Three kinds of inorganics, HNTs, silica and calcium carbonate were used as the fillers for the thermoplastics. A number of organics with hydrogen bonding functionalities, including melamine (MEL), diphenyl guanidine (DPG), 2,4,6-trimercapto-s-triazine (TCY), melamine cyanuric acid (MCA), tri-(2-hydroxyethyl) isocyanurate (THEIC), beta cyclodextrin (Beta-CD), were used. The chemical structures and their hydrogen bonding functionalities of all the organics were tabulated in Table 1. As shown in the table, the hydrogen bonding functionalities such as OH, N, SH are proton donor or acceptor and consequently are expected to easily participate the formation of hydrogen bonds with inorganic fillers.

The mechanical properties of the PP composites with the HNTs and silica as the fillers are summarized in Table 1 and 3 respectively. The data suggests the reinforcement strategy has substantial reinforcement effects on the composites. The flexural properties, especially the flexural modulus, are increased significantly with the incorporation of a number of organics. The incorporation of a number of organics also has contribution to the tensile strength to some extent. However, all the composites containing the organics possess deteriorated impact strength.

The authors believe that, with the incorporation of the organics, the inorganics could be bridged via the hydrogen bonding between the hydroxyl groups on the surfaces of inorganics and hydrogen bonding functionalities of the organics. Once the bridged inorganics structure formed, the mobility of the chains at the interface will be therefore substantially restricted and consequently the composites show much higher rigidity. In addition, the bridged inorganics structure would be beneficial to the transfer of the loaded stress, which also should be responsible for the improved flexural properties and tensile strength.

As discussed above, once the bridged inorganics structure formed, the mobility of the matrix molecules will be confined. When the composites are impacted, the dissipation of impact energy is less effective, leading to the deteriorated impact properties for all the composites. As a consequence, all the composites with the formation of bridged inorganics show lower

**Table 1**  
Organics used for the formation of hydrogen bonds.

Organics	Abbreviation	Molecular structures	Hydrogen bonding functionalities
Melamine	MEL		N, NH <sub>2</sub>
Diphenyl guanine	DPG		NH
2,4,6-trimercapto-s-triazine	TCY		N, SH
Melamine cyanuric acid	MCA		O, N, NH, NH <sub>2</sub>
Tri-(2-hydroxyethyl) isocyanurate	THEIC		O, OH
Beta cyclodextrin	Beta-CD		OH

**Table 2**  
Mechanical properties of PP and PP/HNTs composites (data in the parenthesis is the standard variation).

PP & PP/HNTs composites	Flexural modulus (GPa)	Flexural strength (MPa)	Tensile strength (MPa)	Impact strength (KJ/m <sup>2</sup> )
Neat PP	1.31 (0.06)	43.1 (0.33)	33.4 (0.39)	4.67 (0.29)
PP/HNTs (100/30)	1.75 (0.07)	49.5 (1.23)	31.3 (0.56)	4.28 (0.26)
PP/HNTs/MEL (100/30/1)	2.51 (0.06)	57.3 (0.76)	35.5 (0.47)	3.76 (0.48)
PP/HNTs/MEL (100/30/3.75)	2.65 (0.09)	58.5 (0.96)	35.5 (0.59)	3.55 (0.38)
PP/HNTs/MEL (100/30/7)	2.67 (0.01)	58.0 (1.38)	34.6 (0.34)	3.45 (0.52)
PP/HNTs/MEL (100/30/10)	2.70 (0.03)	57.3 (0.86)	34.4 (1.11)	3.39 (0.05)
PP/HNTs/MCA (100/30/1)	1.97 (0.05)	51.4 (0.13)	33.4 (1.08)	3.73 (0.39)
PP/HNTs/MCA (100/30/3)	2.09 (0.06)	51.9 (0.72)	32.7 (0.52)	3.91 (0.24)
PP/HNTs/MCA (100/30/5)	2.10 (0.04)	51.8 (1.02)	31.7 (1.35)	3.58 (0.03)
PP/HNTs/TCY (100/30/1)	1.98 (0.07)	52.5 (1.46)	32.3 (0.97)	4.22 (0.16)
PP/HNTs/TCY (100/30/2.5)	2.03 (0.05)	52.1 (0.78)	32.0 (0.35)	4.11 (0.36)
PP/HNTs/TCY (100/30/5)	2.01 (0.03)	51.6 (0.52)	31.8 (1.34)	3.96 (0.21)
PP/HNTs/TCY (100/30/10)	2.10 (0.04)	50.8 (0.95)	30.9 (1.16)	3.70 (0.09)
PP/HNTs/betaCD (100/30/2.5)	2.04 (0.04)	53.4 (0.73)	32.2 (1.35)	4.06 (0.42)
PP/HNTs/DPG (100/30/2.5)	1.95 (0.03)	52.4 (1.47)	32.3 (0.46)	3.69 (0.13)
PP/HNTs/THEIC (100/30/2.5)	1.86 (0.08)	50.1 (1.25)	30.7 (0.93)	4.18 (0.31)

toughness. As shown in Fig. 1, the impact fractured surface of the PP/HNTs/MEL composite was rather smooth than that of PP/HNTs composite, indicating the deteriorated toughness of the composites with the formation of hydrogen bonds.

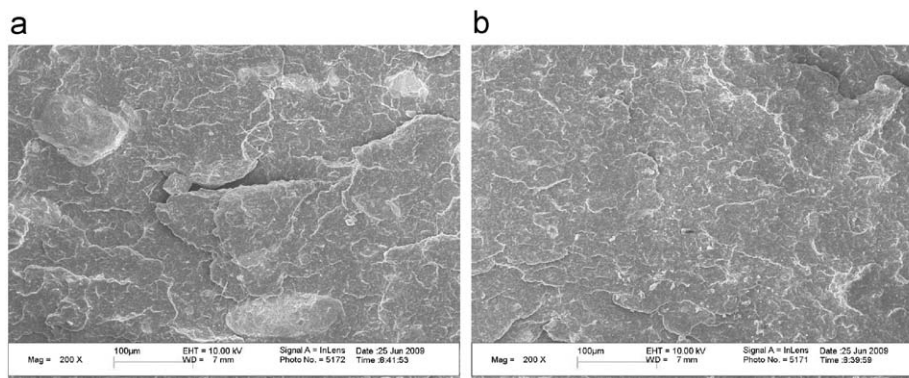
For the comparison purpose, the mechanical properties of the PP composites with calcium carbonate as filler are also summarized in Table 3. It is indicated that there's little reinforcement effect with the incorporation of MEL. This may be due to the ineffectiveness of the formation of bridge among inorganics via

hydrogen bonding as there are few hydroxyl groups on the surface of calcium carbonate, which will be substantiated by below FTIR result.

The effectiveness of the reinforcement strategy in a polar thermoplastics, PA 6, and another non-polar thermoplastics, HDPE, were also investigated and results of the mechanical properties were summarized in Table 4. Similarly, the results suggest that hydrogen bonding bridged inorganics show evident contribution to the reinforcement of PA 6 and HDPE composites.

**Table 3**Mechanical properties of PP, PP/silica composites and PP/CaCO<sub>3</sub> composites (data in the parenthesis is the standard variation).

PP and PP composites	Flexural modulus (GPa)	Flexural strength (MPa)	Tensile strength (MPa)	Impact strength (KJ/m <sup>2</sup> )
Neat PP	1.31 (0.05)	43.1 (1.26)	33.4 (0.56)	4.67 (0.37)
PP/silica (100/10)	1.64 (0.03)	51.5 (0.57)	32.4 (1.12)	4.14 (0.09)
PP/silica/MEL (100/10/0.83)	1.83 (0.03)	53.7 (0.75)	32.8 (0.46)	3.39 (0.21)
PP/silica (100/30)	1.65 (0.05)	50.7 (1.36)	31.8 (1.01)	3.73 (0.14)
PP/silica/MEL (100/30/2.5)	1.92 (0.04)	55.6 (2.16)	33.4 (0.36)	3.14 (0.38)
PP/CaCO <sub>3</sub> (100/10)	1.56 (0.05)	46.7 (1.00)	31.4 (0.66)	5.01 (0.32)
PP/CaCO <sub>3</sub> /MEL (100/10/0.83)	1.61 (0.05)	47.3 (0.27)	31.5 (0.73)	4.68 (0.26)
PP/CaCO <sub>3</sub> (100/30)	1.70 (0.09)	44.2 (0.76)	28.0 (0.46)	4.60 (0.10)
PP/CaCO <sub>3</sub> /MEL (100/30/2.5)	1.76 (0.01)	44.2 (0.46)	26.6 (1.56)	3.95 (0.21)

**Fig. 1.** SEM photo of fractured surface of PP composites: (a) PP/HNTs composites (100/30); (b) PP/HNTs/MEL composites (100/30/2.5).**Table 4**

Mechanical properties of PA 6, HDPE and their composites (data in the parenthesis is the standard variation).

PA 6& PA 6/HNTs composites	Flexural modulus (GPa)	Flexural strength (MPa)	Tensile strength (MPa)	Impact strength (KJ/m <sup>2</sup> )
Neat PA 6	1.93 (0.10)	79.7 (2.10)	62.2 (1.03)	7.45 (0.36)
PA 6/MEL (100/2.5)	2.07 (0.16)	88.0 (1.03)	66.9 (0.74)	8.18 (0.13)
PA 6/HNTs (100/30)	3.16 (0.21)	104.6 (0.06)	60.0 (0.58)	4.52 (0.47)
PA 6/HNTs/MEL (100/30/1)	3.53 (0.02)	107.1 (0.45)	60.9 (0.36)	4.34 (0.13)
PA 6/HNTs/MEL (100/30/2.5)	3.55 (0.05)	112.9 (3.25)	60.1 (0.47)	4.33 (0.36)
PA 6/HNTs/MEL (100/30/7.5)	3.68 (0.08)	110.0 (2.02)	69.6 (0.31)	4.56 (0.26)
PA 6/HNTs/MEL (100/30/10)	3.65 (0.13)	109.1 (1.03)	68.7 (0.28)	4.68 (0.10)
PA 6/HNTs (100/30)	2.86 (0.11)	97.23 (1.02)	53.20 (1.06)	4.92 (0.02)
PA 6/HNTs/MCA (100/30/2.5)	3.45 (0.02)	107.7 (1.33)	50.14 (0.46)	4.48 (0.34)
Neat HDPE	0.69 (0.04)	23.0 (0.55)	20.9 (1.06)	3.13 (0.26)
HDPE/HNTs (100/30)	1.07 (0.16)	27.8 (1.36)	22.1 (0.54)	2.14 (0.35)
HDPE/HNTs/MEL (100/30/2.5)	1.31 (0.08)	30.0 (0.59)	23.3 (0.89)	2.04 (0.24)

In summary, the investigation of mechanical properties of inorganics filled thermoplastics with incorporation of certain organics verified the effectiveness of the reinforcement strategy.

### 3.2. The prerequisites for the formation of bridged inorganics via hydrogen bonding

In the present work, the authors attempted to bridge the inorganics in thermoplastics matrices via hydrogen bonding by the introduction of certain organics. It is therefore required that all the inorganics and the organics used to bridge inorganics contain hydrogen bonding functionalities. As a consequence, the inorganics and organics contain hydrogen bonding functionalities are the prerequisites for the bridge of inorganics via hydrogen bonding.

Generally, most of the inorganics are hydrophilic and abound of hydroxyl groups on their surfaces [10,11]. The hydroxyl groups could be used for the formation of hydrogen bonding. In the present work, two kinds of inorganics abound of hydroxyl groups on their surfaces and a kind of inorganics lacking of hydroxyl groups on its surface are utilized. The inorganics abound of hydroxyls include the HNTs, a kind of naturally occurring nanotubes, and precipitated silica. As indicated in Fig. 2, HNTs have lumen structures, with the inner and outer diameter of about 15–20 and 40–50 nm respectively. HNTs have been disclosed as a new kind of inorganic modifier for improving the mechanical and thermal properties of polymers [12,13]. Calcium carbonate, lacking of hydroxyl groups on its surface, was used as the control [14]. Fig. 3 is the FTIR spectra of the HNTs, precipitated silica and calcium carbonate. The absorptions around 3500 cm<sup>-1</sup> are assigned as the stretching vibration of hydroxyl groups,

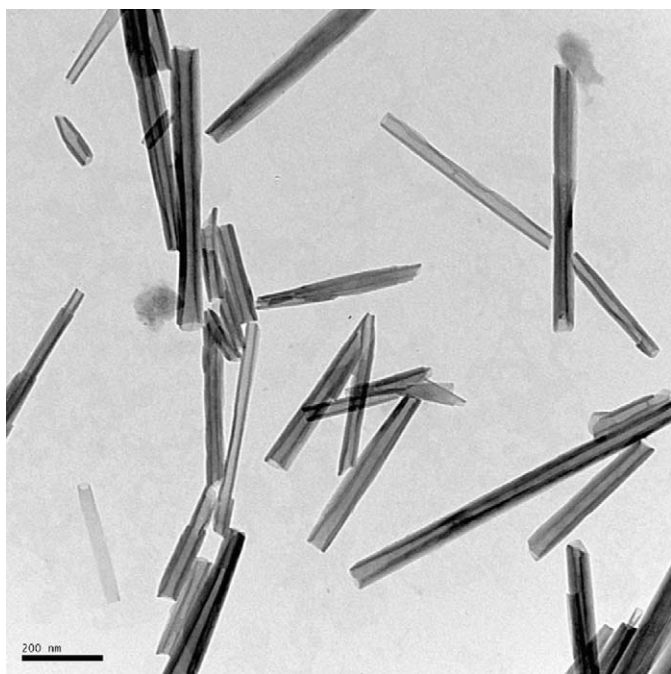


Fig. 2. TEM photo of HNTs.

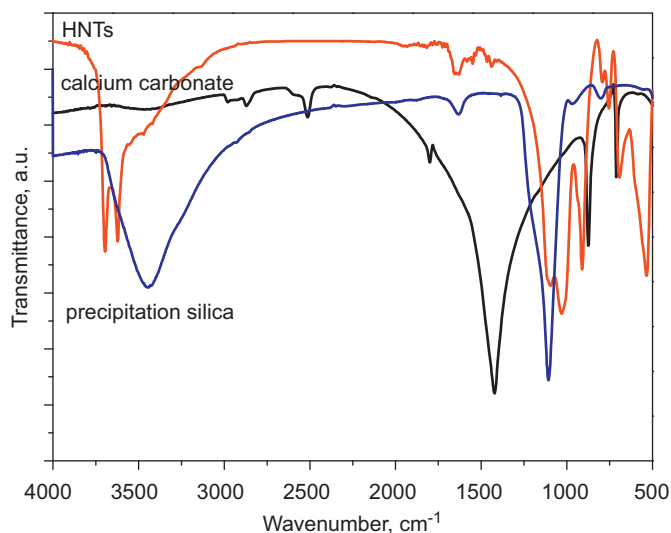


Fig. 3. FTIR spectra of HNTs, precipitated silica and calcium carbonate.

suggesting abundant of hydroxyl groups on the surface of HNTs and precipitated silica and, however, few of hydroxyl groups on the surface of calcium carbonate. To effectively bridge the inorganics and alleviate the aggregation of inorganics containing hydrogen bonding functionalities, adding certain organics with hydrogen bonding functionalities are necessary. The added organics facilitate the dispersion of the inorganics and bridge the better dispersed inorganics. This is another prerequisite for the formation of bridged inorganics via hydrogen bonding. The results of the above mechanical properties of the three types of thermoplastics composites have substantiated the prerequisites for the formation of bridged inorganics via hydrogen bonding.

### 3.3. Characterizations of the formation of the bridged inorganics via hydrogen bonding

Generally, for the crystalline and semi-crystalline polymers, it is believed the variation in crystallinity have tremendous effects on the mechanical properties [15–17]. In the present investigations, the crystallinities of PP, PA6 and their composites were determined by DSC method. As indicated in Table 5, there is little change in the crystallinities among the neat thermoplastics and all their composites. As a consequence, the improvement in modulus should not be attributed to the change in crystallinity.

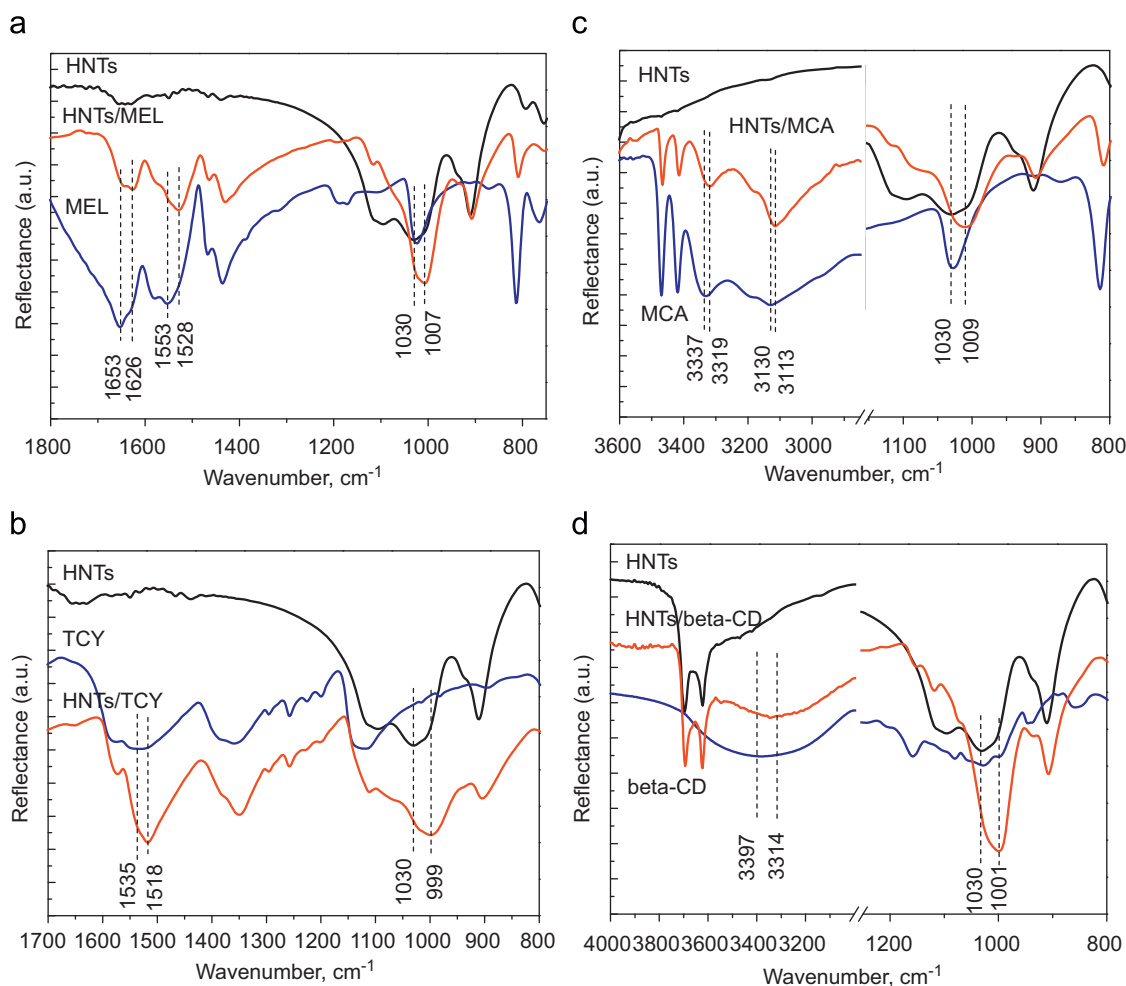
As mentioned above, the authors attribute the reinforcement of thermoplastics to the bridged inorganics via hydrogen bonding in the matrix. FTIR is often used to characterize the formation of hydrogen bonding [18–20]. In the present investigations, as the content of organics containing hydrogen bonding functionalities in the composites are relatively low, in addition, the existence of thermoplastics matrices may interfere the observation of the FTIR absorptions related to the formation of hydrogen bonding, therefore, it is rather difficult to characterize the formation of hydrogen bonding in the composites by FTIR. To verify the formation of hydrogen bonding, ATR-FTIR experiments were performed on the model mixtures only containing the inorganics and the organics to examine the formation of hydrogen bonding by ATR-FTIR experiments and the results were discussed as follows.

Fig. 4 shows the FTIR spectra of HNTs, MEL, TCY, MCA, beta CD and their mixtures respectively. The mixture was prepared by blending HNTs with organics at a speed of 10 000 rpm. The absorption around  $1030\text{ cm}^{-1}$  is assigned as the absorption of Si–O stretching vibrations [21,22]. However, there is a blue shift from  $1030$  to  $1007\text{ cm}^{-1}$  for the absorption of Si–O stretching vibrations in the mixture, which should be resulted from the formation of hydrogen bonding in hydroxyl groups on the surfaces of HNTs. The absorptions around  $1653$  and  $1553\text{ cm}^{-1}$  in MEL are assigned as the N–H bending and side chain asymmetric C–N stretching in MEL respectively [23]. Both the two absorptions also have a blue shift in the spectra of the HNTs/MEL mixture, suggesting the formation of hydrogen bonding in MEL molecules. In the mixture of HNTs and TCY, absorption around  $1535\text{ cm}^{-1}$  is assigned as the symmetric and asymmetric vibrations of NCS system as shown in Fig. 4 [24]. As mentioned above, the peak around  $1030\text{ cm}^{-1}$  is assigned as the absorption of Si–O stretching vibrations. Similarly, the formation of hydrogen bonding in the mixture causes a blue shift of the two peaks. In the MEL absorptions around  $3337$  and  $3130\text{ cm}^{-1}$  are assigned as N–H symmetric stretching and N–H...N stretching vibrations respectively [23]. The blue shift of the two absorptions and the absorption of Si–O stretching vibrations around  $1030\text{ cm}^{-1}$  also indicate the formation of hydrogen bonding between HNTs and MCA. Again, the blue shift of absorptions assigned as the vibrations of O–H group and Si–O stretching in HNTs/beta CD mixture also occurs, suggesting the formation of hydrogen bonding in the model mixture of HNTs and beta CD.

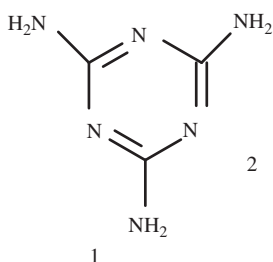
In order to further substantiate the formation of hydrogen bonding in the PP/HNTs/MEL composites, XPS survey was performed. As the nitrogen in the MEL is the hydrogen bonding functionality, the XPS survey aims at the variation of bonding energy of nitrogen in MEL molecules, for the formation of hydrogen bonding would induce the change of bonding energy of the nitrogen. As shown in Fig. 5, there are two kinds of nitrogen in the molecule of melamine due to the difference of chemical environment, which are marked with 1N and 2N respectively. The XPS results of the two samples were presented in Figs. 6 and 7, in addition, the detailed bonding energies of nitrogen are also summarized in the figures.

**Table 5**  
DSC results of PP, PA 6 and their composites.

Samples	Crystallinity (%)	Samples	Crystallinity (%)
Neat PP	46.7	Neat PA 6	25.8
PP/HNTs (100/30)	47.2	PA 6/MEL (100/2.5)	25.3
PP/HNTs/MEL (100/30/1)	48.0	PA 6/HNTs (100/30)	23.6
PP/HNTs/MEL (100/30/3.5)	47.9	PA 6/HNTs/MEL (100/30/1)	21.7
PP/HNTs/MEL (100/30/5)	47.3	PA 6/HNTs/MEL (100/30/2.5)	22.3
PP/HNTs/MEL (100/30/7.5)	47.1	PA 6/HNTs/MEL (100/30/7.5)	23.1
		PA 6/HNTs/MEL (100/30/10)	24.8



**Fig. 4.** ATR-FTIR spectra of HNTs, MEL, TCY, MCA, beta CD and their mixture: (a) HNTs, MEL and their mixture; (b) HNTs, TCY and their mixture; (c) HNTs, MCA and their mixture; (d) HNTs, beta CD and their mixture.



**Fig. 5.** Chemical formula of melamine.

Fig. 6 shows the bonding energy of nitrogen in the MEL molecules and in the composite obtained at lower-resolution respectively. Compared with the bonding energy of N 1s in the

MEL molecules, the bonding energy of N 1s in the composite has an evidently shift, from 396.0 to 400.1 eV, which suggesting the formation of hydrogen bonding in the composite.

High-resolution XPS survey of nitrogen in the two samples was performed to get more information in detail, and the results were shown in Fig. 7. The spectra of nitrogen were deconvoluted using ORIGIN 7.0 software into two peaks according with the two kinds of chemical environment in the MEL molecule. The peaks at 396.6 and 396.2 eV are assigned as 1N 1s and 2N 1s respectively [26]. Similarly, the high-resolution XPS suggests that both kinds of nitrogen are contributed to formation of hydrogen bonding in the composite, for the bonding energy of the two kinds of nitrogen both have an evident shift of 1N 1s and 2N 1s, from 396.6 to 400.5 eV and 396.2 to 399.4 eV respectively. It is believed that the protonation of N would induce its bonding energy become higher [25,27,28].

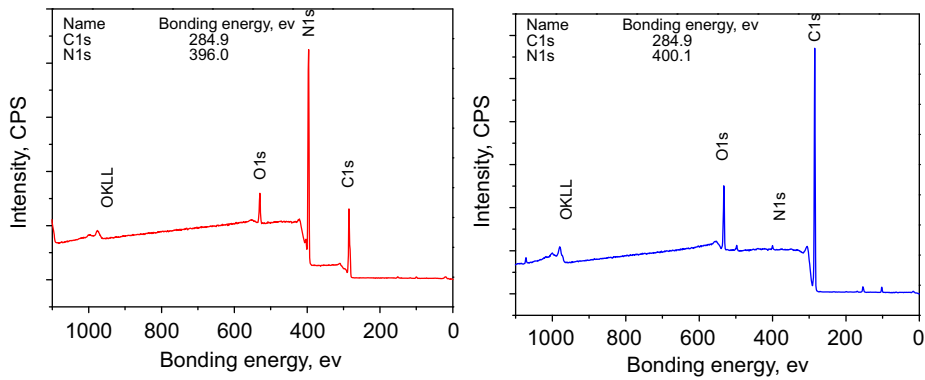


Fig. 6. Low-resolution XPS spectra of MEL (left) and PP composite (right).

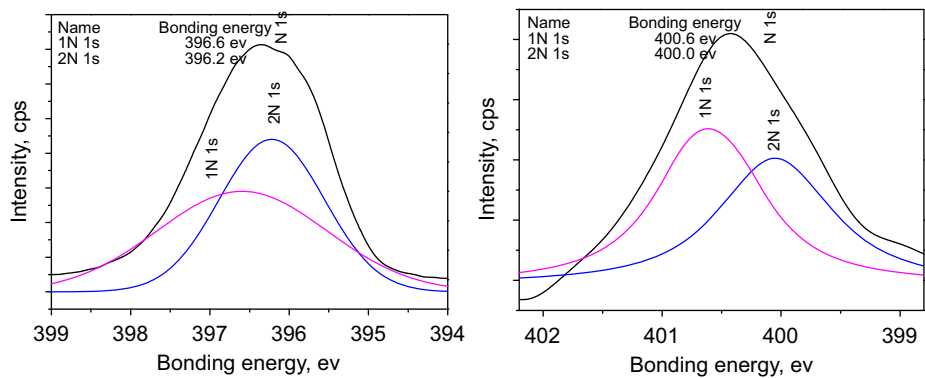


Fig. 7. High-resolution XPS spectra of nitrogen in MEL (left) and PP composite (right).

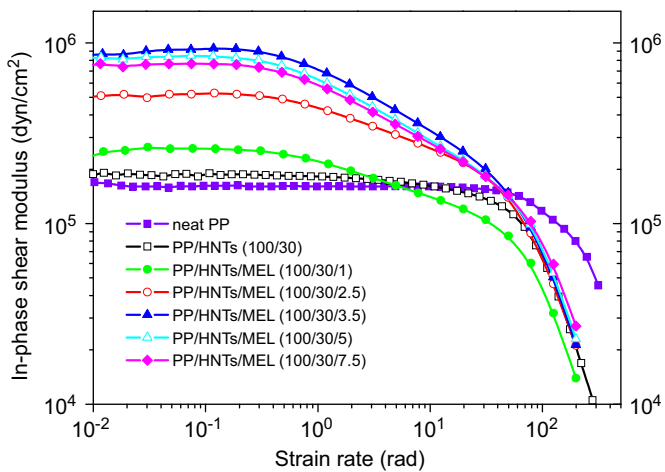


Fig. 8. Variation of in-phase modulus with shear strain rate of PP and PP composites.

To further validate the existence of bridged inorganics via hydrogen bonding in the thermoplastics matrix, the dynamic rheological measurements of the melts of PP and PP composites were performed. Fig. 8 shows the variation of in-phase shear moduli of neat PP, PP/HNTs composite and PP/HNTs/MEL composites with the increase of strain rate. In the low strain stage, the in-phase shear modulus of PP/HNTs composite is slightly higher than that of neat PP. PP/HNTs/MEL composites with appropriate content of the organics, however, show much higher in-phase shear moduli compared with neat PP. The authors ascribe this phenomenon to the hydrogen bonding interaction among inorganics in the PP matrix. Once the hydrogen bonding among

inorganics is formed, the constitutive mobility of PP segments would significantly be restricted due to the entanglement between bridged HNTs and PP segments. As a consequence, the in-phase shear moduli of PP/HNTs/MEL composites are considerably increased. At higher strain rate, the in-phase shear moduli of the PP/HNTs/MEL composites start to decrease dramatically and overlap with those of the other composites at higher strain rate, indicating the breakdown of the hydrogen bonding interactions.

The morphologies of the PP/HNTs composite and PP/HNTs/MEL composite are shown in Fig. 9. The nanotubes are dispersed disorderly in the PP matrix. The rings in the photos are the cross-sections of the tubes which are perpendicular to the observation direction. As indicated in Fig. 9, the dispersion of HNTs in the composite containing MEL is more uniform than the one without MEL. For the composite without MEL, the HNTs tend to self-aggregate via hydrogen bonding in the matrix due to the presence of surface hydroxyl groups. Once the organics containing hydrogen bonding functionalities is added, the hydroxyl groups on the surface of HNTs would combine with the organics via hydrogen bonding, avoiding the self-aggregation of HNTs, and consequently the dispersion of HNTs in PP matrix is improved (Fig. 9).

#### 4. Conclusion

The inorganics could be bridged in thermoplastics matrices via hydrogen bonding with the incorporation of certain organics containing hydrogen bonding functionalities. The hydrogen bonding bridged HNTs led to substantially increased flexural properties. The coexistence of inorganics and organics containing hydrogen bonding functionalities was the prerequisite for the formation of the bridged inorganics via hydrogen bonding. The

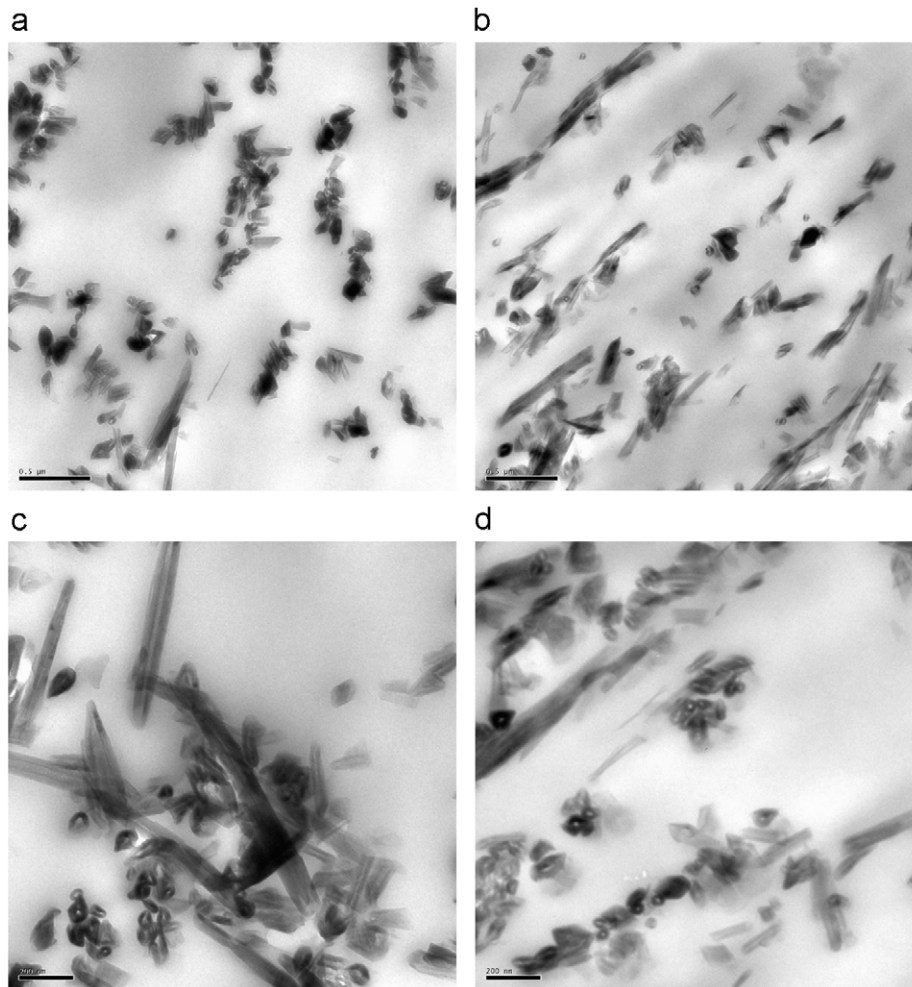


Fig. 9. Morphology of PP/HNTs composites and PP/HNTs/MEL composites (a), (c): PP/HNTs composites (100/30); (b), (d): PP/HNTs/MEL composites (100/30/2.5).

results of ATR-FTIR and XPS results suggest the formation of hydrogen bonding among the inorganics and organics in the composites. Measurements of rheological behavior of PP composites further substantiated the existence of the bridged inorganics.

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