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SHORT COMMUNICATIONS

Formation of Reinforcing Inorganic Network in Polymer *via* Hydrogen Bonding Self-Assembly Process

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Since come into being, polymer materials are getting more and more widely used in every corner of the world. However, some intrinsic shortcomings, such as relatively lower modulus, flammable to fire and inferior thermal stability, restrain the further application of polymer materials, especially for engineering purpose.[1] As a consequence, reinforcing and improving the thermal properties are always the hot topic in polymer material area.

Reinforcing polymers with inorganic particulates is one of most popular strategies as it possesses a number of advantages such as easily processible, relatively lower cost and possible improvements in other properties including thermal stability.[2–5] As early as in 1940s, it was found that, during the studies of dynamic properties of rubber, there was a sharp decrease of modulus with increasing strain in the strain sweep of carbon black filled vulcanizates.[6–10] The phenomenon has been extensively investigated by many researchers. Payne *et al.*[11–15] showed that typically the carbon blacks in rubber formed rod-like structure *via* van der Waals attraction forces, and the rod-like structure then formed into secondary network. The decrease of shear modulus was due to the breakdown of the carbon black network. Further, Payne *et al.*[11] studied clay-rubber system and found the similar behavior like carbon black filled rubbers, which indicated the decrease in modulus with strain was also attributed to the breakdown of the three dimensional filler aggregates network. Even later in rheological studies on clay colloidal, formation of three dimensional structures in aqueous and solvent media were also suggested.[16]

Formation of filler network in plastics was also reported. For example, there is a threshold of percolation in carbon black filled polyethylene which finds applications in positive temperature coefficient (PTC) materials.[17–19] The formation of filler network in polymer matrix, which is responsible for different behaviors, is widely reported.[20–29] The reinforcing of plastics *via* formation of inorganics network, however, has not been well recognized although the reinforcing effects of inorganics on plastics are widely reported. Traditionally, the effectiveness of reinforcing with inorganics is believed to depend on the interfacial bonding between the inorganics and polymer matrix and dispersion state of the inorganics.[30–32]

Reinforcing semi-crystalline polymers, especially polyolefins such as PP with inorganics is challengeable. The difficulties originate principally in the great polarity discrepancy between the polymer and the inorganics. In addition, the filler will facilitate or retard the crystallization process, which may strengthen or weaken the reinforcing effects of the inorganics on the polymer and hence makes the reinforcement uncontrollable.[33–35] Development of the reinforcing strategy irrespective of the polarity discrepancy is highly desirable.

Filled polymers have the stress transfer mechanism similar to that of the fiber reinforced polymeric composites in which the stress is principally transfer by the polymeric matrix.[36–38] The reinforcement especially the modulus, is therefore, sensitive to the interfacial bonding between the polymer and the filler. If the stress transfer is partially transferred by fillers themselves, the reinforcement will not be so much dependent on the interfacial properties and the compatibility or polarity discrepancy will not be so crucial to the reinforcement.

To accomplish this target, the whole strong filler network must be constructed in the polymer matrix. The invariably presence of hydroxyl groups on the inorganics surface provides the possibility of construction filler network *via* hydrogen bonding.

In the present work, the authors attempt to construct filler network in crystalline plastics *via* hydrogen bonding self-assembly process. Specifically, we use naturally occurred halloysite nanotubes (HNTs) and silica as the inorganic hydrogen-bonding couplers (IHC) and several organic species including melamine (MEL), melamine cyanurate (MCA) and diphenyl guanidine (DPG) as the organic hydrogen-bonding couplers (OHC) as they provide specific sites for donating or accepting unpaired electrons. The pair of IHC and OHC forms strong inorganic network *via* hydrogen bonding in the polypropylene during processing. The improvements in mechanical properties were evaluated. The possible origins for the improvements were examined and discussed.

EXPERIMENTAL

Materials

The isotactic PP was manufactured by Lanzhou Petrochemical incorporation, with a melt flow index of 2.84 g/10 min (after ISO-1133: 1997(E)). The halloysite nanotubes (HNTs), grade of Ultrafine, were provided by Imerys Tableware Asia Limited, New Zealand. The specific area is approximately 28 m^2/g.

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Melamine (MEL), melamine cyanurate (MCA) and guanidine are commercially available chemical grade reagents and used as received.

Preparation of the Composites and Characterizations

Preparation of the Composites The PP composites were prepared with a twin-screw extruder. The temperatures setting from the hopper to the die were 180/200/200/200/200/200 °C. The screw speed was 100 rpm, and the pelletized granules of PP were dried for 5 h under 80 °C. Then granules were injection molded to the specimens for mechanical determinations at 200 °C.

Dynamic Rheological Measurements Rheology measurements 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 0.05–600%. The measurements were performed at 180 °C and the frequency was set as 10 rad/s.

X-Ray Photoelectron Spectra X-Ray photoelectron spectra of MEL and HNTs/MEL mixture (well mixed powder under vigorously stirring) were recorded by using an X-ray Photoelectron Spectrometer (Kratos Axis Ultra DLD) with an Aluminum (mono) K_α source (1486.6 ev). The Aluminum K_α source was operated at 15 kV and 10 mA. The samples were mounted onto a holder with double-sided adhesive tape and placed in a vacuum in the range 10^{-8}–10^{-7} torr. The analyzed sample area was approximately 0.7×0.3 mm. 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.

Attenuated Total Refraction Fourier Transform Infrared Spectroscopy (ATR-FTIR) HNTs powder, and mixtures of HNTs and MEL 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 cm^{-1} wavenumbers.

Transmission Electron Microscopy (TEM) The specimens of PP/HNTs composites with and without melamine were ultramicrotommed into thin pieces of about 120 nanometers in thickness with Leica EM UC6. TEM observations were done using JEM-100CXII TEM machine at an accelerating voltage of 30 kV.

Differential Scanning Calorimetry (DSC) DSC data was measured by a NETZSCH DSC204 F1 using nitrogen as purging gas. The samples 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 is cooled down to 40 °C at rate of 10 °C/min. The exothermic flows were recorded as a function of temperature. The crystallinity was calculated based on the endothermic enthalpy (ΔH_f) as follows:

$$Crystallinity(\%) = \frac{\Delta H_f}{\Delta H_f^0 \times C}$$

Where ΔH_f and ΔH_f^0 are the endothermic enthalpies of the sample and the PP with crystallinity of 100% respectively. C is the PP weight percentage in the composite.

Determinations of Flexural Moduli Flexural moduli of the composites were measured according to ISO 178: 1993 with a Instron 4465 Universal tester.

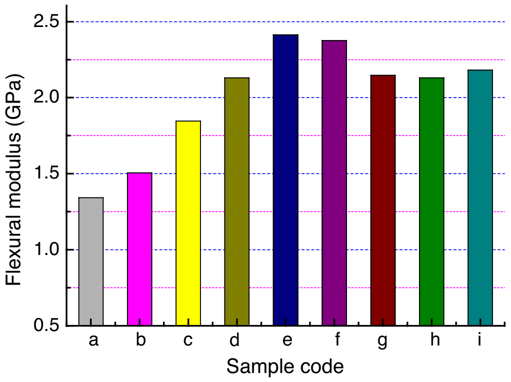

Figure 1. Effects of inorganics network on flexural modulus of PP/HNTs composite. (a) neat PP; (b) PP/MEL (100/5); (c) PP/HNTs (100/30); (d) PP/HNTs/MEL (100/30/1); (e) PP/HNTs/MEL (100/30/2.5); (f) PP/HNTs/MEL (100/30/5); (g) PP/HNTs/MEL (100/30/10); (h) PP/HNTs/MCA (100/30/10); (i) PP/HNTs/DPG (100/30/2.5). (Figures in the parentheses are the weight ratio of the components.)

Polarization Microscopy Observations (PMO) The morphologies of the crystallites of the composites were recorded with an Olympus BX41 polarized optical microscopy.

RESULTS AND DISCUSSION

The results of the flexural modulus are present in Figure 1. It is clear that the inclusions of all the OHC are beneficial to the improvement in the modulus. Inclusion of 30 phr HNTs into PP leads to 37.5% improvement in modulus. In addition, incorporation of 4.8 wt. % MEL into PP (Sample B) has no substantial effects on the modulus. Surprisingly, incorporation of small amount (*ca.* 2 wt. %) of MEL (d) in the control sample (b) results in substantial increase in modulus. The modulus of the sample d is 80% higher than that of the neat PP. Although MCA and DPG are less significantly than MEL, the inclusions of the two OHC are also effective in improving the modulus. As the formed inorganics network is relatively rigid, it may survive only at small deformation and it may break down before yielding or failure of the material. Indeed, not shown here, the effects of the formation of the inorganics network on the other mechanical properties such as tensile strength and impact strength are less profound. The experiments also indicate that the OHC themselves are incapable in altering the properties of the PP. For example, inclusion of the same amount of MEL into PP results in negligible changes in mechanical properties.

Therefore a hypothesis of self-assembling of HNTs network in presence of OHC *via* hydrogen bonding during processing is proposed to interpret the above results. The presence of nitrogen atoms and/or protons in OHC molecules provides the donors or acceptors of unpaired electrons. During the processing, the HNTs are finely dispersed in PP matrix under strong shearing force. The dispersed HNTs are intimately contacted with the molecules of the OHC to form network *via* hydrogen bonding. A question would then be naturally raised. Is the OHC necessary for the formation of hydrogen bonded network? The key for the answer is to understand the differences in scale of IHC and OHC and spatial arrangement of hydrogen bonding couplers. Many so-called nanosized inorganics tend to aggregate into larger particles typically with diameter ranging from 50 nm to several micrometers. As a consequence, the formation

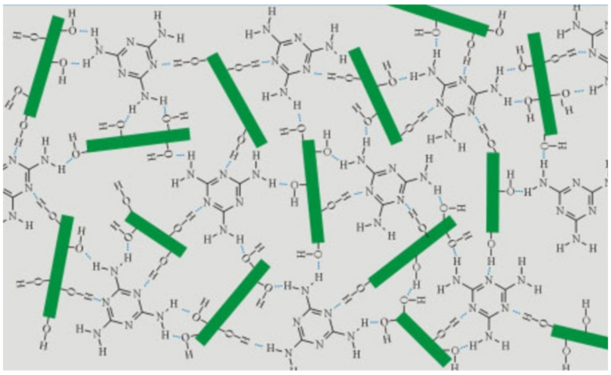

Figure 2. Scheme of the self-assembling process *via* hydrogen bonding.

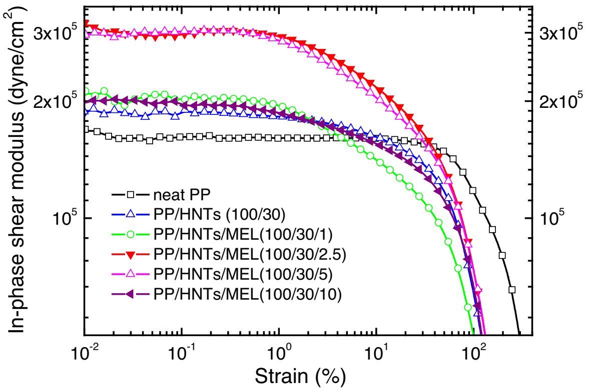

Figure 3. Variation of in-phase modulus with shear strain of the three systems.

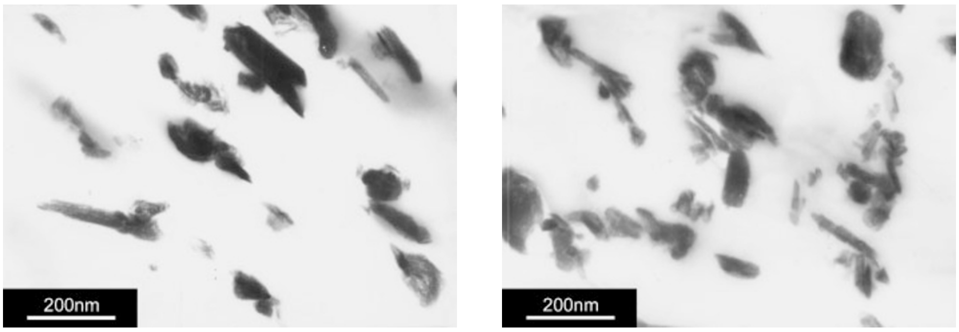

Figure 4. TEM photos of PP composites (left) PP/HNTs (100/30); (right) PP/HNTs/MEL (100/30/2.5).

of network structure by the IHC themselves is less possible as they are not easily be contacted each other at usual concentration. Once the OHC is used, the OHC not only possesses smaller size and more importantly it may occupy the void among the IHC and sever as a multi-arm hinge to assemble the IHC. This effect of OHC is analogous to that of water in the formation of particle clusters *via* hydrogen bonding in silica colloid.[39]

Experiments on alternative inorganics such as silica also show the similar positive effect of hydrogen bonding network on the mechanical properties. As expectedly, the inorganics without abundant hydroxyl groups such as calcium carbonate[40] is incapable of forming the hydrogen bonding network as indicated by the practically unchanged properties. The formation of hydrogen bonding is schematically shown in Figure 2. In this scheme, the IHC may be dispersed at different scale, from nanometer to micrometer.

To validate the hypothesis that formation of hydrogen bonding network in the PP matrix, the dynamic rheological measurements of the melt of the composites and the FTIR-ATR of the mixtures of HNTs and OHC were performed.

Figure 3 shows the variation of in-phase shear modulus of PP and PP composites with the increase of strain. 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 OHC content, however, show much higher in-phase shear modulus compared with neat PP. As suggested by Figure 4, the HNTs dispersed in the PP matrix in the form of aggregates. The aggregates decrease the constitutive mobility of PP segments under flow state. The in-phase shear modulus of the PP/HNTs composite is therefore slightly higher than that of the neat PP. Although the TEM (Figure 4) reveal slightly better dispersion of HNTs for the sample of PP/HNTs/MEL composite, the in-phase shear modulus of the PP/HNTs/MEL composites with appropriate MEL content is substantially higher than those of the neat PP and PP/HNTs composite. We ascribe this phenomenon to the formation of hydrogen bonded HNTs network in the PP matrix. Once the network is formed, the constitutive mobility of PP segments would significantly be restricted. As a consequence, the in-phase shear modulus of PP/HNTs/MEL composite is considerably increased. It should be noted that the in-phase shear modulus of the PP/HNTs/MEL composite is strongly dependent on the MEL content. At insufficient OHC content, the network could not been fully constructed. At excessive OHC content, however, the excessive OHC tends to cover on the surface of the IHC and this may also retard the formation of the network. As a consequence, there is a critical OHC content for the formation of the hydrogen bonded network. As expectedly, the PP/HNTs/MEL composites show optimal flexural modulus at the critical MEL content. At higher stain, the in-phase shear moduli of the composites with network structures start to decrease dramatically and overlap with those of the other composites, indicating the breakdown of the network structure.

Generally, the formation of hydrogen bonding would induce the change of bonding energy characterized XPS.[41–43] As a consequence, XPS survey of neat MEL and HNTs/MEL mixture were performed to identify the formation of hydrogen bonding. In the present investigation, nitrogen element was chosen to examine the formation of hydrogen boning for its higher sensitivity. As shown in Figure 5, sorted by chemical environment, there are two kinds of nitrogen in the molecule of melamine, which are traced with 1N and 2N respectively. The XPS results of the two samples were presented in Figures 6 and 7, in addition, the detailed bonding energies of nitrogen are also summarized in the figures.

Figure 6 shows the surface elemental compositions and their bonding energy of the MEL and the mixture of HNTs/MEL obtained at lower-resolution respectively. Compared with MEL, the bonding energy of N 1s in the mixture of HNTs/MEL has an evidently shift, from 396.0 eV to 399.5 eV, which are attributed to the formation of hydrogen bonding in the mixture.

To get more detained information, high-resolution XPS survey of nitrogen in the two samples were performed and the results were shown in Figure 7. The spectra of nitrogen were deconvoluted using ORIGIN 7.0 software into two peaks as there are two kinds of chemical environment in the MEL molecule. The peaks at 396.6 eV and 396.2 are assigned as 1N 1s and 2N 1s respectively.[44] Similarly, the higher-resolution XPS suggests that formation of hydrogen bonding have significant effects on the bonding energy of nitrogen, which induces a evident shift of 1N 1s and 2N 1s, from 396.6 eV to 400.5 eV and 396.2 eV to 399.4 eV respectively. It is believed that the protonation of N would induce its bonding energy become higher.[41,45,46] Consequently, as suggested by XPS results, it is believed that hydrogen bonding is formed between the IHC and the OHC.

FTIR is convenient to characterize the formation of hydrogen bonding between molecules.[47–51] Typically, the formation of hydrogen bond would cause red or blue shift of the absorptions for the groups neighboring the hydrogen bonds.[47–51] In order to eliminate the disturbance of PP molecules in the FTIR investigation, the ATR-FTIR of the HNTs and HNTs/MEL mixtures were performed and the results are presented in Figure 8. The peaks between 1000 cm^{-1} and 1150 cm^{-1} are assigned to the absorption of Si-O stretching vibrations. With the incorporation of MEL, it is evidently that there is successive blue shift for Si-O absorption. The result suggests that hydrogen bonding is formed in the mixture of HNTs and MEL.

The variation in crystallinity is another possible origin for the change in modulus for the semi-crystalline polymers. But the determination of the crystallinity by DSC method suggests that there is little change in crystallinity among the neat and all the composites, ranging from 45.9% to 47.8%. As a consequence, the improvement in modulus should not be attributed to the change in crystallinity. As the whole inorganics network is formed in the PP matrix, the growth of spherulite would be

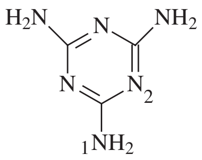

Figure 5. Chemical formula of melamine.

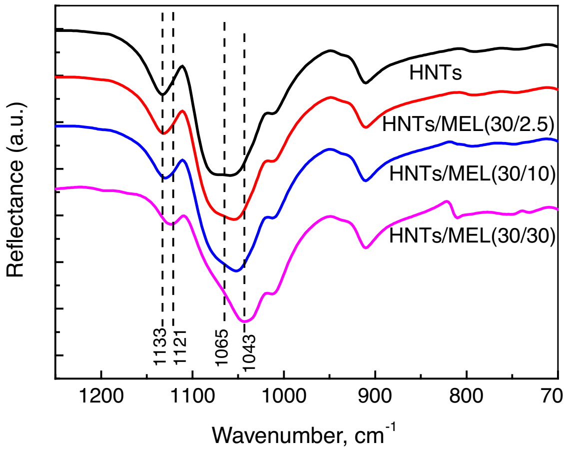

Figure 8. ATR-FTIR spectra of HNTs and mixtures of HNTs/MEL.

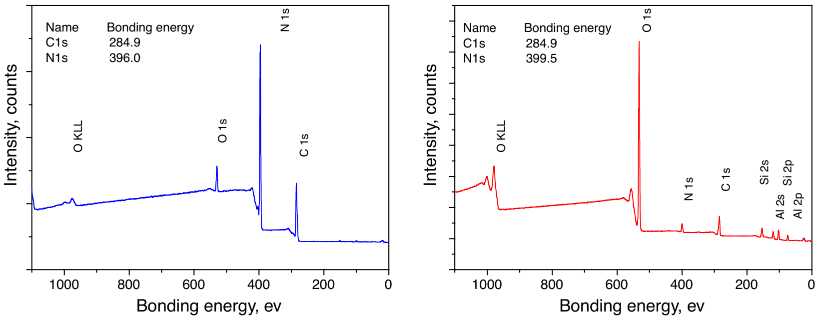

Figure 6. Low-resolution XPS spectra of MEL (left) and HNTs/MEL (right).

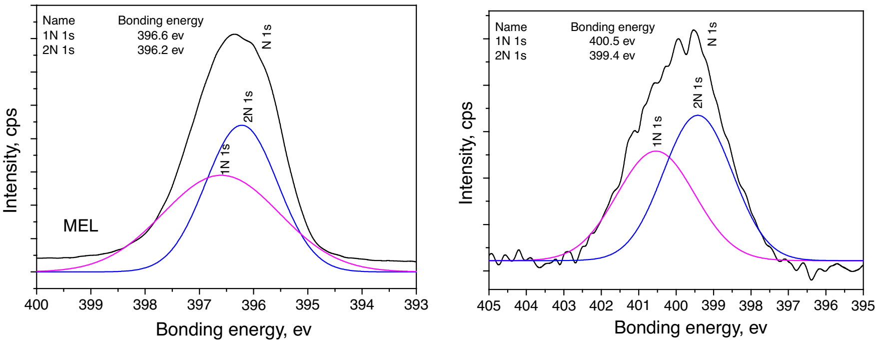

Figure 7. High-resolution XPS spectra of nitrogen in MEL (left) and mixture of HNTs/MEL (right).

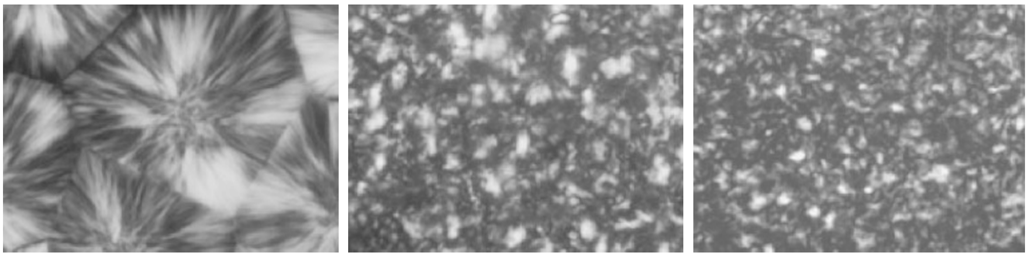

Figure 9. PMO photos of PP, PP/HNTs (100/30) composite PP/HNTs/MEL composite (100/30/2.5) (from left to right).

restricted. As shown in Figure 9, the size of the spherulites of PP/HNTs composite is reduced due to the nucleation effects of inorganics. For the PP/HNTs/MEL composite, the size of the spherulite is further reduced due to the restriction of the formed inorganics network.

CONCLUSION

In summary, we show the inorganics network in polymer may be constructed *via* hydrogen bonding self-assembly process with inorganic hydrogen-bonding coupler (IHC) and organic hydrogen-bonding couplers (OHC). The pair of IHC and OHC forms strong inorganic network *via* hydrogen bonding in the polymer during processing. By this methodology, the flexural modulus are improved up to 80% due to an optimal combination between IHC and OHC and hydrogen bonding between IHC and OHC use the effect of the properties as supplements. This work provides a general method for reinforcing polymer, especially the nonpolar semi-crystalline polymer using inorganics, which possesses characteristics such as "green process," unsophisticated, easily scale-up, cost competitive etc, irrespective of the great polarity discrepancy between the polymer and the inorganics.

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