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A change of phase morphology in poly(*p*-phenylene sulfide)/polyamide 66 blends induced by adding multi-walled carbon nanotubes

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Abstract

By adding a small amount of acid treated multi-walled carbon nanotubes (MWCNTs) into poly(*p*-phenylene sulfide)/polyamide 66 (60/40 w/w) blends, the morphology was found to change from sea–island to co-continuous structure. As the MWCNT content was increased, the morphology came back to sea–island but with increased domain size. It was very interesting to note that the MWCNTs were found to be selectively located in the PA66 phase, and their assembling determines the final morphology of PPS/PA66 blends. A dendritic contacted MWCNTs network was formed at low load, which leads to the formation of a co-continuous structure, and isolated MWCNT aggregates were observed at high load, which leads to the formation of sea–island morphology. Since the properties of multiphase polymeric materials are not only determined by the properties of the component polymers, but also by the morphology formed, our work indicates that the behavior of phase-separating polymer blends containing MWCNTs can be exploited to create a rich diversity of new structures and useful nanocomposites.

Keywords: Carbon nanotubes; Microstructure; Blend

1. Introduction

Both theoretical and experimental studies have shown that carbon nanotubes (CNTs) have extremely high tensile moduli and tensile strengths. The break strength of CNTs is reported as high as 200 GPa and elastic modulus is in the 1-TPa range [1–3]. Carbon nanotubes have a thermal conductivity of about double that of diamond and electric-current-carrying capacity 1000 times higher than copper wire [4]. So there exists a great deal of potentiality in using CNTs as a reinforcing agent for polymer matrices. However, the dispersion of CNTs in polymer matrices is always a key issue to achieve high performance [5–10].

Some unique structures and properties have been found by incorporating CNTs in polymers due to its special structure and assembling property. Yuezhen et al. [11] obtained highly oriented polyethylene filled with aligned carbon nanotubes from solutions. Kwangsok et al. [12] found that CNTs in the multi-walled nanotube (MWNT)/polystyrene/poly(methyl methacrylate) blend thin film were dispersed on the silicon substrate without any aggregation and formed two-dimensional nano-wire arrays. Pötschke et al. have studied the morphology [13], electrical [14] and rheological [15] properties of polycarbonate (PC)/MWCNT composites and obtained a notable reduction in volume resistivity for a PC/polyethylene blend by addition of 0.41 vol% MWCNT. A ‘pseudo-solid-like’ behavior standing for a network structure has been reported by McNally et al. [16]. Fangming et al. [17] investigated the network in the CNTs/poly(methyl methacrylate) nanocomposites by the linear viscoelastic behavior and electrical conductivity. Some recent works focused attention on the effects of nanoparticles, such as organoclay [18] and CNTs [19], on altering microstructure of polymer blends, and thus affecting ultimate performances. In poly(ethylene terephthalate)/poly(vinylidene fluoride) blends [20], a triple-continuous structure in the CNT-filled polymer blend was formed where CNT segregates in the

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continuous PET phase, forming a continuous conductive path, resulting in a material with an electrical short circuit. A similar phenomenon was also found in the CNTs/PA6/ABS blends [21].

In this article, we reported our efforts to manipulate the phase morphology of PPS/PA66 blends using CNTs. By adding a small amount of acid treated MWCNTs into PPS/PA66 (60/40 w/w) blends, the morphology was found to change from sea–island to co-continuous structure; as the MWCNT content increased, the morphology changed back to sea–island but with increased domain size. MWNTs were selectively dispersed in the PA66 phase, and their assemblings determined the final morphology of PPS/PA66 blends.

2. Experimental section

Poly(*p*-phenylene sulfide) (PPS) in a powder form ($M_w = 4.8 \times 10^4$, melting temperature = 285 °C) was purchased from Sichuan Deyang Science Tech. Shareholding Company. Polyamide 66 (PA66) ($M_w = 2.0 \times 10^4$, melting temperature = 250 °C) was supplied by Shenma Company. Multi-walled carbon nanotubes (MWCNTs) were provided by the Chengdu Institute of Organic Chemistry of the Chinese Academy of Science (Chengdu, China). MWCNTs were synthesized through the dissociation of methane at a high temperature of 700 °C with a NiO/La_2O_3 catalyst [22]. The outer and inner diameters of MWCNTs were 10–20 and 5–10 nm, respectively. They were washed with concentrated hydrochloride acid for the removal of the catalyst and its carrier and then purified with concentrated HNO_3 for the removal of amorphous carbon particles. It is also well known that CNTs can be solubilized through chemical modification or functionalization by the chemical oxidation in aqueous media [23–29].

The powders of PPS, PA66 and MWCNTs were first dry-mixed together by physical mixer. Melt blending of PPS/PA66 with fixed composition (60/40 w/w) with different content of MWCNTs was conducted using a co-rotating twin-screw extruder (TSSJ-25, ChenGuang, Ltd. Chengdu, China). In all extrusion processes, the hopper temperature was set as 160 °C; the barrel was divided into three parts and the counterpart temperatures were set as 270, 290, 290 °C, respectively; the die temperature was 280 °C. The screw speed was maintained at about 120 rpm. After melt extrusion, a series PPS/PA66/MWCNT composites were obtained, in which MWCNT content varied from 0.001 to 1 phr. It should be noted that 'phr', which is the abbreviation of 'part per hundred of resin', means the weight percent of filler to 100 units weight polymer matrix, for example, in this study the weight ratio of PPS/PA66/MWCNTs (0.5 phr CNTs) is 60/40/0.5. For comparison purpose, blend without MWCNTs was also prepared by melt extrusion with the same parameters individually. The extruded strands were then palletized and dried at 85 °C. The resulted pellets were injected into a mold with aid of a PS40E5ASE injection machine (NISSEI, Tokyo, Japan) with barrel temperature 275–300 °C and injection pressure of 900 kg cm^{-2}.

SEM experiment was carried out to examine the phase morphology. The samples were fractured in liquid nitrogen and etched. The etched surfaces were then gold coated and investigated in an SEM instrument, JEOL JSM-5900LV SEM (Jeol JSM-5900LV, Tokyo, Japan) with an acceleration voltage of 20 kV. For overseeing the morphology of blends two etched methods, namely chemical etching and physical etching were used to compare PPS, PA66 and MWCNTs. For PPS/PA66 binary blends, chemical etching was performed by immersion of the fractured specimens in formic acid (10 min, room temperature), which dissolved the PA66 phase selectively. For PPS/PA66/MWCNT ternary composites, the physical etching was carried out, in which the fractured surface of the specimen was subjected to argon ion bombardment at 500 eV. The beam was focused perpendicularly to the surface of the specimens. Depending on the different resistances of the components to the ion beam etch (MWCNTs > PPS > PA66), the phase morphology and the location of the MWCNTs in the blend can be studied by this method [30].

3. Results and discussions

3.1. Morphological change with increasing MWCNT content

PPS is an high performance engineering plastic. Its applications are limited due to the poor impact property and high price. It is often blended with PA66 for a balanced mechanical properties and cheaper price. These two polymers are immiscible though their solubility parameters are similar [31]. At fixed ratio of 60/40 (w/w), PPS/PA66 blend shows typical sea–island morphology, as shown in Fig. 1(a). The dark area shows the removed PA66 phase with an average size of 0.5 μm. Thus PA66 forms the droplet and PPS forms the continuous matrix. This sea–island morphology is determined by their viscosity ratio and volume ratio. However, by adding small amount of MWCNTs, the phase morphology changes from sea–island to co-continuous like structure, as shown in Fig. 1(b–f), the content of MWCNT is 0.001, 0.01, 0.05, 0.1, 0.3 phr, respectively. Comparing these SEM photographs with Fig. 1(a), one can find that many individually dispersed spheres of PA66 phase have coalesced into one huge domain with anisotropic profile, implying at least that a quasi-continuous phase of PA66 is formed within PPS matrix after incorporation of small amount of MWCNT. Very interestingly, this co-continuous like morphology does not hold any longer with further increasing the content of MWCNTs. As shown in Fig. 1(g and h), by increasing the content of MWCNTs to 0.5 and 1 phr, the phase morphology returns back to the original sea–island structure but with bigger domain size of PA66. The average size of the dispersed PA66 becomes 1 μm and 2 μm, respectively. It should be noted that the change of phase morphology of PPS/PA66 blends (60/40 w/w) was caused by very small amount of MWCNTs. Here the minimum of 0.001 phr of MWCNTs was used. Due to the limitation of experimentation, it is difficult to prepare composite contained less content of MWCNTs accurately.

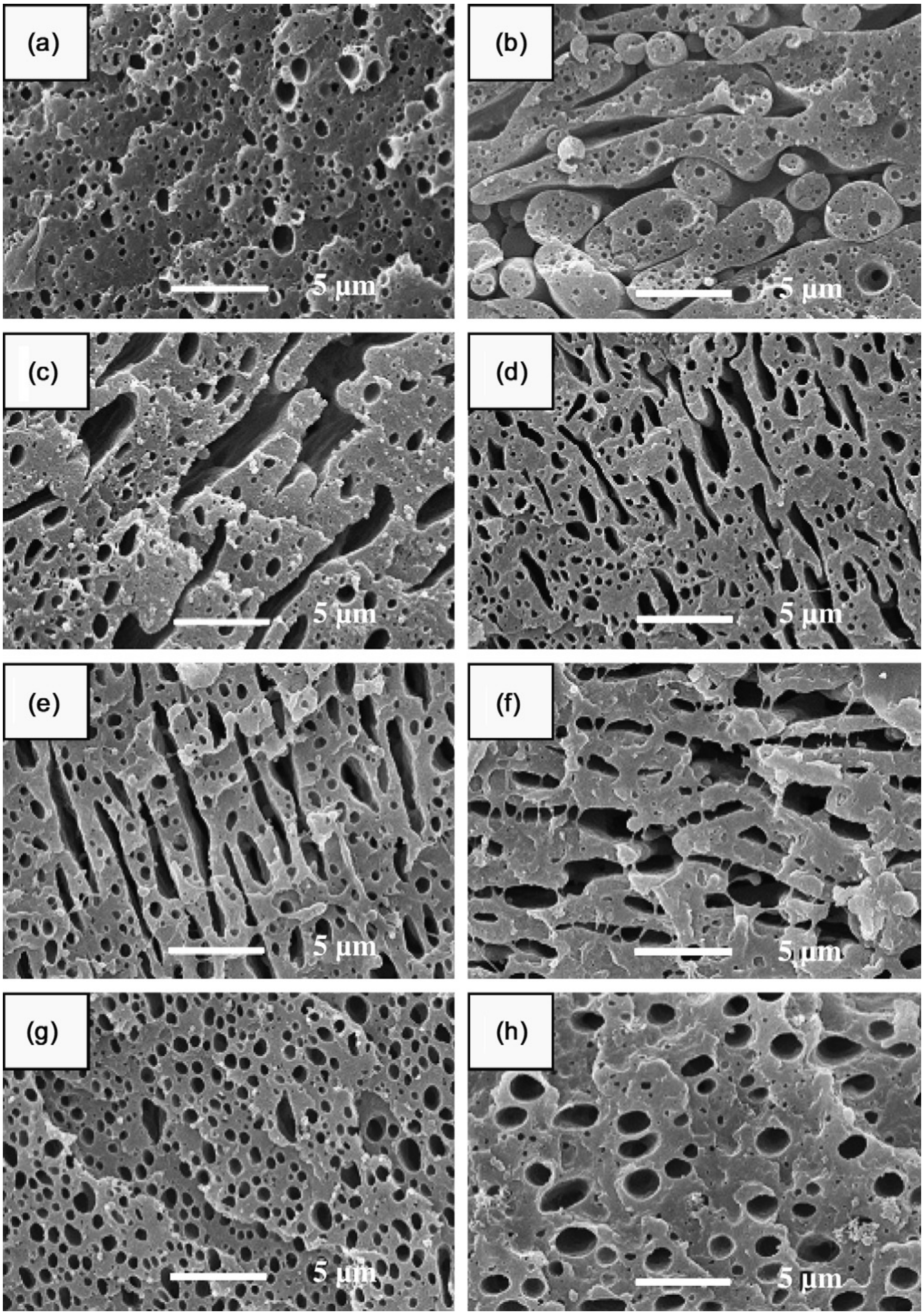

Fig. 1. SEM photos of composites with varying MWCNTs content endured injection mold: (a) without MWCNTs; (b) with 0.001 phr MWCNTs; (c) with 0.01 phr MWCNTs; (d) with 0.05 phr MWCNTs; (e) with 0.1 phr MWCNTs; (f) with 0.3 phr MWCNTs; (g) with 0.5 phr MWCNTs; (h) with 1 phr MWCNTs.

3.2. Location and morphology of MWCNTs in the nanocomposites

The key to understand the change of phase morphology by adding MWCNTs is to know its location and morphology in the blend system. For this reason, a new etching method named ion beam etching was introduced, based on the different resistances of the components to the ion beam (MWCNTs > PPS > PA66). Since it is hard to distinguish PA66 phase from PPS basal phase under TEM observation after chemical staining with OsO_4, the ion beam etching seems to be one of few available means to differentiate ternary components unambiguously. As an example, Fig. 2 shows the SEM photograph of blend containing 0.01 phr MWCNTs after ion beam etched. The PA66 phase is darker than the PPS phase, and the MWCNTs can also be seen in this way. In the area A in Fig. 2, a kind of skeleton can be formed by some sidelong MWCNTs. And in the area B, some heads of MWCNTs are exposed.

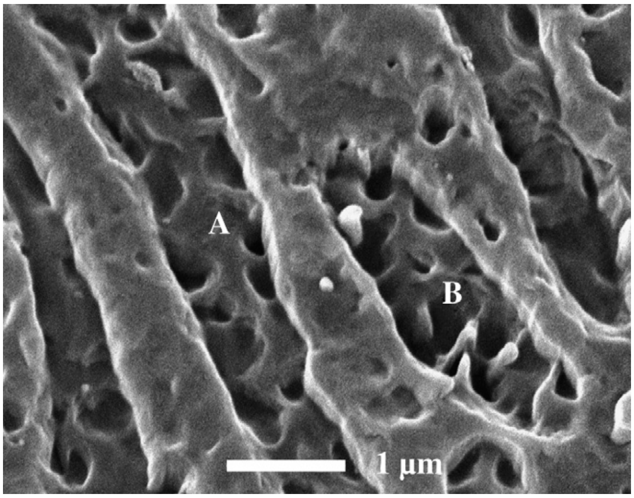

Fig. 2. SEM photos of PPS/PA66/MWCNT nanocomposites (0.01 phr MWCNTs) after ion beam etched.

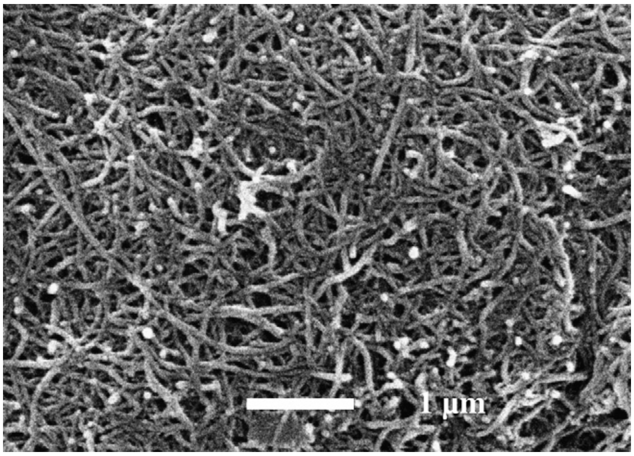

Fig. 4. SEM photo of raw MWCNTs.

Now it is clear that all the MWCNTs are located exclusively in the PA66 phase. The next work is to examine the dispersion of MWCNTs in the PA66 phase. It is very difficult because the content of used MWCNTs is so small. To realize this aim, samples with different MWCNT contents were placed in a semi-permeable bag and extracted by formic acid, in which both PA66 and PPS phases were dissolved, and the MWCNTs reminded and could be precipitated out on the wall of semi-permeable bag. The extraction lasted for 168 h and every 8 h the formic acid was renewed. At last, the remains in the semi-permeable bag were washed by using distilled water and were collected. After complete drying, the collected powders were observed under SEM. Fig. 3a and b shows the photographs of collected powders from sample with 0.01 phr MWCNTs. The dendritic-like objects that are stacked together in the view represent the continuous PA66 phase. In contrast, spheres with rough surface are observed in the sample with 1 phr MWCNTs (Fig. 3c and d). The shape observed in these two samples is entirely different from the original MWCNTs (Fig. 4) and is covered completely with PA66 polymer. The similar phenomenon was also reported by Lee et al. in a recent work and ascribed as due to the mixing-induced interaction [32].

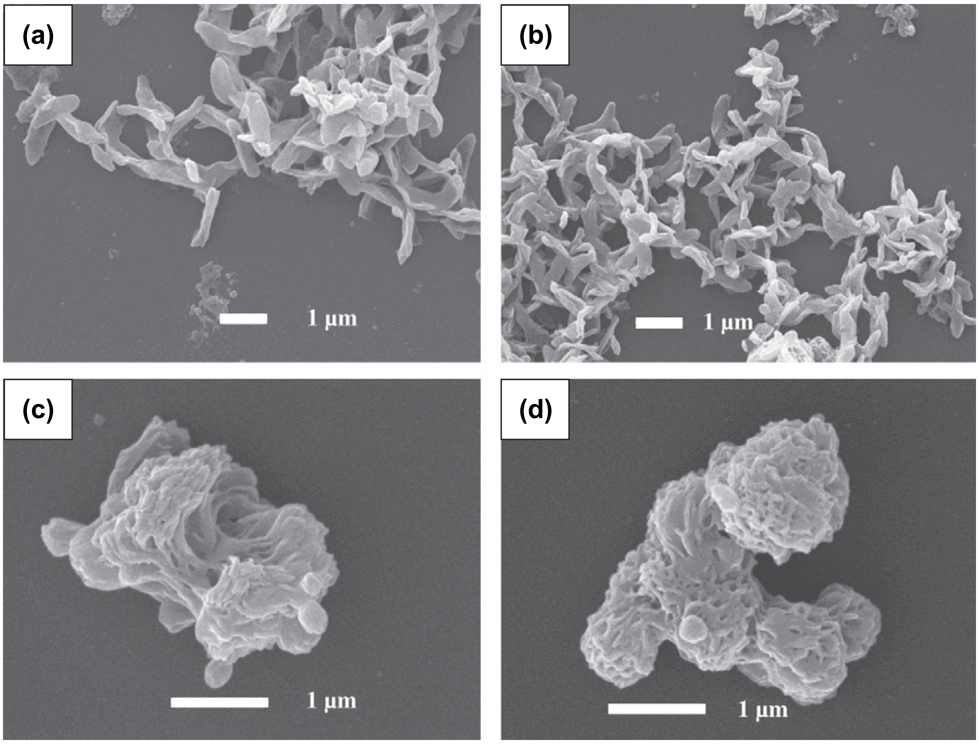

Fig. 3. SEM photos of extracted productions from the nanocomposites: (a) and (b) with 0.01 phr MWCNTs; (c) and (d) with 1 phr MWCNTs.

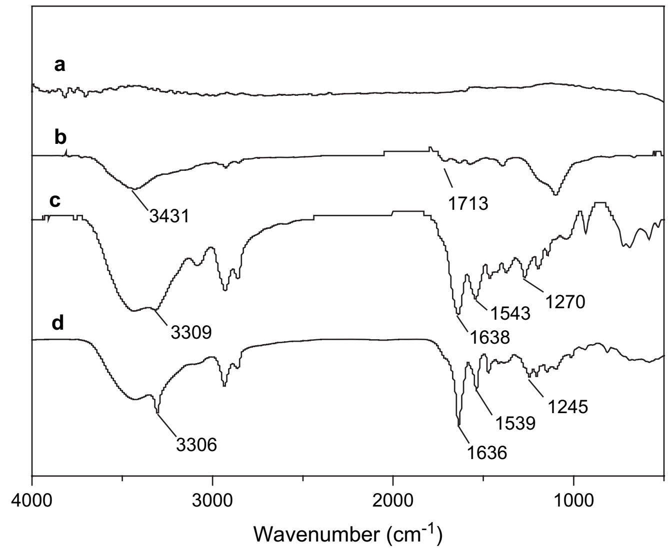

Fig. 5. FTIR spectra of extracted productions from the nanocomposites and MWCNTs: (a) raw MWCNTs; (b) HNO_3 treated MWCNTs; (c) PA 66; (d) extracted productions.

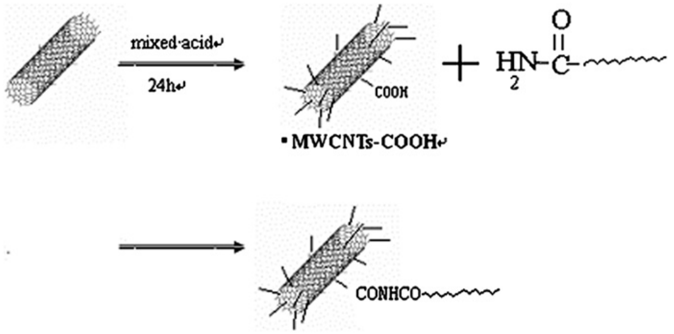

Fig. 6. Chemical reaction illustration during the sample preparation.

3.3. FTIR spectra characterization

To approve the mixing-induced interaction between MWCNTs and PA66, the FTIR spectra of the MWCNTs, acid treated MWCNTs, PA66, and the extraction collected powders were carried out, and are shown in Fig. 5. The FTIR spectra of the extraction collected powders (in Fig. 3a) have the same character peak at 3300 cm^{-1} (which belongs to NH function group), 1640 cm^{-1}, 1550 cm^{-1} and 1282–1250 cm^{-1} (which belong to amide function group) with PA66. So it can be conclude that this congeries should be MWCNTs covered with PA66. The PA66 which is physically absorbed on MWCNTs should be dissolved completely in such a long extraction time, so there must be some chemical bonding between MWCNTs and PA66. The FTIR spectra of acid treated MWCNTs show that they have carboxyl peak at 1713 cm^{-1} and the pristine MWCNTs without any obvious function group. It means that acid treatment could introduce carboxyl group into MWCNTs. And the carboxyl function group will react with NH function group of PA66 and forms the chemical interlinking. The mechanisms of the potential chemical reaction are illustrated in Fig. 6. This is also the reason of MWCNTs being located in PA66 phase selectively.

3.4. Unique mechanism of phase morphology assembling in PPS/PA66 blends induced by adding MWCNTs

By chemical bonding between polar groups, the assembling of MWCNTs in PPS/PA66 matrix could be fixed after the extraction. In other words, the morphology of the extraction collected powders should represent the assembling of MWCNTs in PPS/PA66/MWCNT composites. Obviously, the phase morphology of PA66 is intimately related to assembling

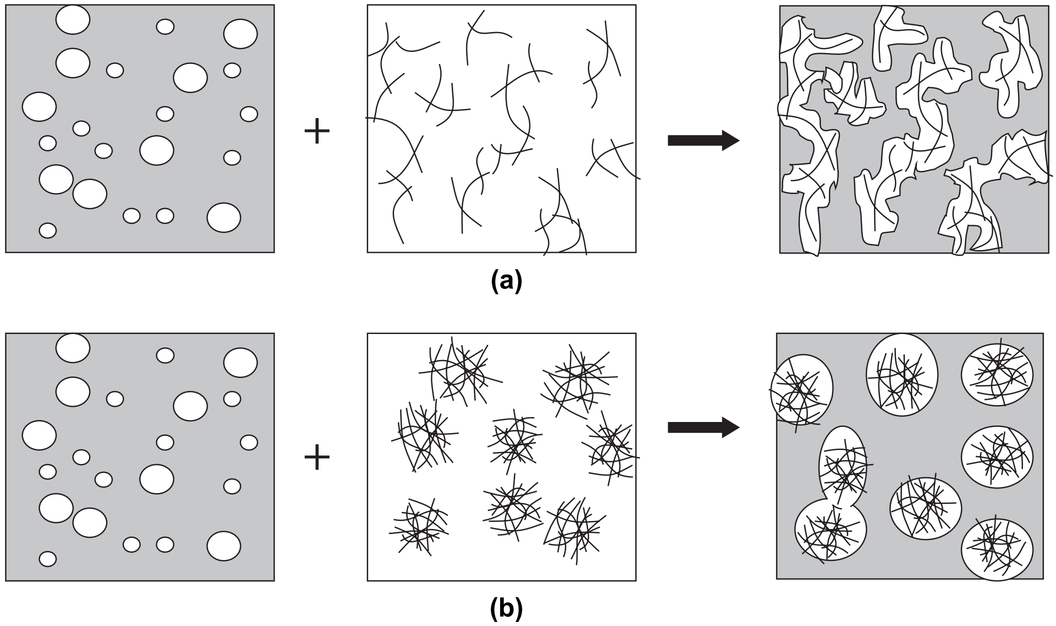

Fig. 7. Schematic representation of the PPS/PA66 (60/40 w/w)/MWCNTs nanocomposites morphology changing: (a) low load MWCNTs (<0.5 phr) disperse evenly and form a percolating network; (b) high load MWCNTs (>0.5 phr) aggregate like clews.

of MWCNTs' congeries. When the content of MWCNTs is small and forms the dendritic structure, the corresponding PA66 phase absorbed on it is continuous; while increasing the content of MWCNTs, the aggregation of MWCNTs occurs and forms sphere-like shape, PA66 phase changes to sea–island morphology. Most interesting thing is, at that time, the profile of PA66 absorbed on CNTs becomes the droplet phase. Thus both the shape and the size of the MWCNTs' congeries determine the PA66 phase in the composites.

Interestingly, the MWCNTs could form some chemical bonds with PA66 and serve as framework for leading the formation of PA66 phase in the composite system. Many researches have indicated that the well-dispersed MWCNTs could form such kind of network. In the MWNT/polystyrene/PMMA composites, the MWCNT network was directly ascertained by SEM and AFM [12]. And the rheology testing was adopted for determining the 3-D network in the MWCNT/polymer nanocomposites [15]. Also a lot of works have evidenced that MWCNTs are easy to aggregate together at a higher content [33]. The mechanism of phase morphology assembling in PPS/PA66/ blends induced by adding MWCNTs is shown in Fig. 7. When the content of MWCNTs is low (less than 0.5 phr here), the MWCNTs will form dendritic structure and contact with each other, thus the PA66 absorbed on it forms the continue phase (co-continuous structure). The MWCNTs would aggregate like clews when the content of MWCNTs is high (above 0.5 phr here), thus the PA66 phase absorbed on it forms sphere structure (sea–island structure).

4. Conclusion

The morphology of PPS/PA66 blends (60/40 w/w) with various amounts of MWCNTs has been investigated carefully. It is found that the MWCNTs are selectively located on the PA66 phase. At low load, the well-dispersed CNTs will form dendritic edge-touched network structure, resulting in a co-continuous structure. At high loading, the MWCNTs aggregate like clews, resulting sea–island morphology. This can be a new way to create a rich diversity of new structures and useful nanocomposites.

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