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Formation of cylindrical phase structure in PMMA/HBP polymer blend films

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Abstract

The evolution of the phase separation was investigated for poly(methyl methacrylate)(PMMA)/hyperbranched poly(ester-amide)(HBP) blend films on glass substrate by means of phase contrast microscopy. The films with different component ratios show different phase separation processes and phase morphologies. At a film thickness of about several hundreds nanometers, a cylindrical dispersed phase was observed in the films with lower HBP content. The effects of the composition and sample thickness on the formation of the special morphology were also studied. It is found that the interaction between the substrate and HBP and the thickness of blend film are essential factors for the formation of the phase morphology and the appearance of the special cylindrical morphology depends on the component ratio and the film thickness. There is a critical film thickness, above which the special morphology could be observed. The critical thickness varies as the HBP weight percent changes. Our research provides a possible strategic way to obtain polymer films with special structure which are important for an increasing number of applications in wide fields.

Keywords: Blend films; Cylindrical structure; Hyperbranched poly(ester-amide)

1. Introduction

Polymer and polymer blend films have attracted considerable attention because of their wide applications in many fields such as photoresists, dielectric layers, adhesives, microelectronic and optoelectronic devices. Due to the intrinsic immiscibility of most polymer blends, polymer mixtures usually demix during the extraction of solvents. The phase separation morphologies [1–8] and dynamics [9–15] of polymer blend films have been studied extensively during the last decade. Compared to the bulk, the phase separation process of a polymer blend film is strongly influenced by the presence of a substrate. Varying the strength of the interactions between the substrate and the polymers can lead to different ultimate phase separation morphologies. Bruder et al. [1] studied spinodal decomposition of blend thin films of deuterated polystyrene and poly(styrene-*co*-4-bromostyrene) on different substrates, and found a bilayer of two bulk phases could change to a column structure when changing the substrate from a chromium-plated silicon wafer to an oxide layer. Stefan et al. [2] used atomic force microscopy (AFM) to investigate the domain structures in thin films of an immiscible polystyrene/poly(methyl methacrylate) blend after spin-coating. The normal and lateral organization of the phase-separated domains is governed by a complex interplay between preferential aggregation of one phase at the substrate and phase segregation in the film. It is widely accepted that the polymer composition with a lower surface energy will segregate at a lower surface energy substrate during the phase decomposition process. Since, the experimental convenience for obtaining polymers and substrates with different surface energies, our and other groups' previous work [2–4,6–8,16,17] have generally revealed the role which surface and interface energies played in the evolution of phase morphology.

Recently, many researches [18–23] focused on patterned substrate, attempting to use different interactions between polymer components and patterned substrate, to attain controlled phase morphology on it. However, adjusting the interactions between polymer components and substrate is an effective way to control the ultimate phase morphology. Changing the interfacial interaction between components in polymer blend and substrate by varying the functional groups in polymer helps to modulate the phase morphology.

Hyperbranched polymers (HBP) are highly branched polymers with densed functional groups in the end of the branches which are prepared through a one-step polymerization process. The chemical and physical properties of hyperbranched polymer are determined by the shape and multiplicity of the core and building block, and by the size and

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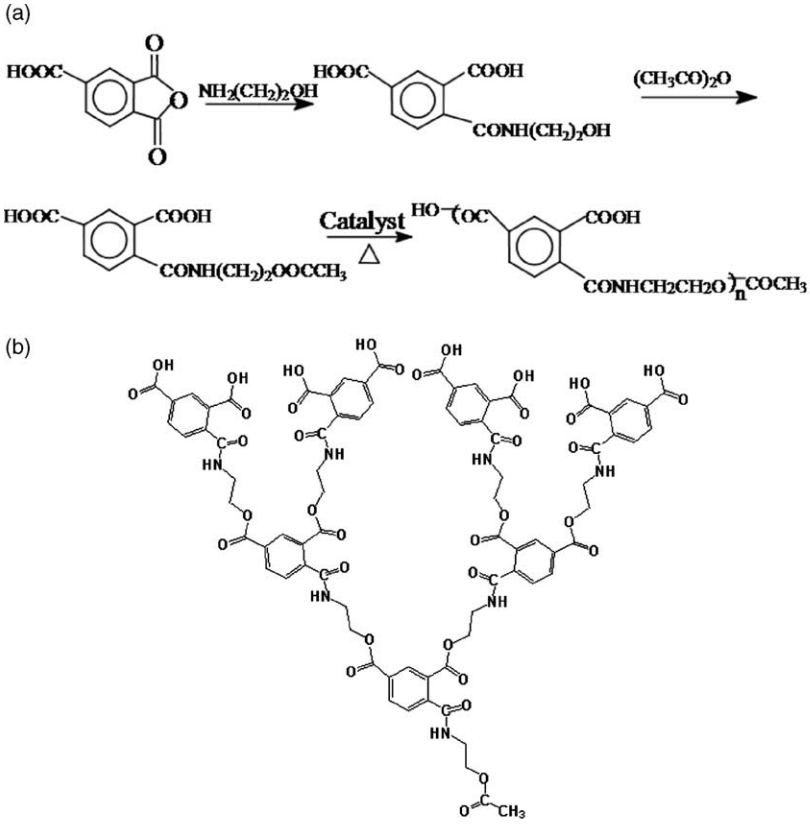


Fig. 1. (a) Synthesis scheme of monomer and corresponding polymer. (b) Sketch of a third-generation HBP molecule.

shape of terminal groups, as well as their chemical composition. These compact three-dimensional sphere molecules with high density of functional terminal groups offer potential applications as tougheners, sensors, self-assemblies, biochemicals and so on [24–33]. Joshua et al. [34] have studied the surface segregation of polyetherimide HBPs with different surface energies in blends with polystyrene.

In this paper, a hyperbranched polymer, poly(ester-amide) with terminal carboxyl acid groups was synthesized by bulk polycondensation of *N*-(2-acetoxyl ethyl)-*N*-(2′,4′-dicarboxylic benzoyl) amine in our laboratory. We prepared the blend films using the hyperbranched polymer mixed with poly(methyl methacrylate) by spin-coating from a common solution. The enhanced interfacial interaction between the HBP in the blend and the glass substrate can be achieved. We want to reveal the effects of HBP's characteristic properties and the interfacial interaction between the blend film and the glass substrate on the formation of phase morphology above the glass transition temperatures of both polymers by means of phase contrast microscopy and atomic force microscopy.

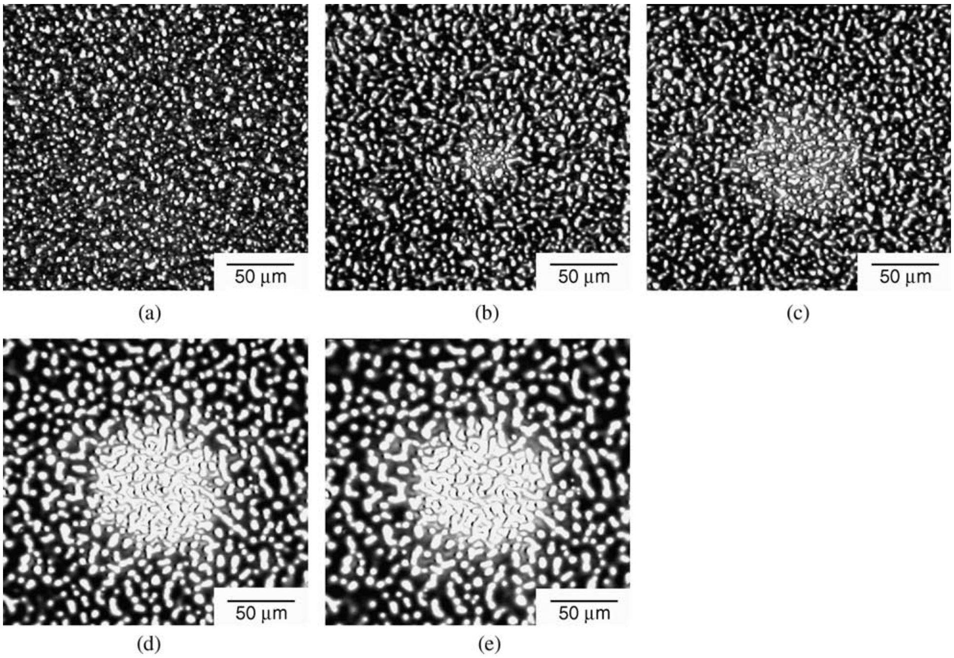
2. Experimental section

2.1. Materials

Poly(methyl methacrylate) (PMMA) used in this work ($M_w = 136{,}600$, $M_w/M_n = 1.56$) was commercially available from Asahi Company and used as received without further purification. A pseudo AB_2 monomer, *N*-(2-acetoxyl ethyl)-*N*-(2′,4′-dicarboxylic benzoyl) amine, was synthesized based on 1,2,4-benzenetricarboxylic anhydride, ethanolamine and acetic anhydride. Hyperbranched poly(ester-amide) with terminal carboxyl acid groups (HBP) used in this work was synthesized by bulk polycondensation of the monomer at 220 °C in a high yield of 92%. The synthesis scheme of monomer and corresponding polymer and a sketch of a third-generation HBP molecule are illuminated in Fig. 1. The details of the synthesis process were reported elsewhere [35]. As reported by Hahn et al. [36], though the two carboxyl groups in a pseudo monomer had different activities, a hyperbranched polymer still could be synthesized from the monomer. The degree of branch is smaller than 0.5 and the actual value is different to obtain. The hyperbranched poly(ester-amide) used here can be easily dissolved in a basic solution. It testifies that there are a lot of carboxyl groups in the HBP molecule. The structure of HBP was characterized by IR, ^{1}H NMR, DSC and TGA. $M_n = 7300$, $T_g = 108$ °C, $T_d = 396.3$ °C.

2.2. Sample preparation

Polymer blend films were prepared by spin-coating from a PMMA/HBP solution (5% (w:v)) on glass substrates. The common solvent for the blends was *N*,*N*-dimethyl formamide (DMF). The weight percents of PMMA in the blend films varied from 90 to 10%. These blends are denoted as 90/10, 80/20, 70/30 and so on. The film thickness was controlled by varying the rotation speed during spin-coating. In order to measure the thickness of films, we scratched several grooves in



(a) (b) (c)

(d) (e)

Fig. 2. Micrographs of the phase morphologies of a PMMA/HBP(80/20) blend film on glass substrate annealed at 230 °C. The annealing time was: (a) 0 min; (b) 2 min; (c) 4 min; (d) 10 min; (e) 25 min. The thickness of the film for Fig. 2 through Fig. 5 is 456 nm.

the surfaces of the films to bare the substrates. MICRO-MEASURE surface profiler (STIL CHR150) was used to measure the average heights of the grooves.

2.3. Phase contrast microscopy

Sample annealing was carried out on a heating stage at 230 °C. The film was kept at 230 °C for certain minutes to allow phase separation to proceed and then the film was rapidly quenched to room temperature by removing them from the heating stage and placing them onto a metal plate. Micrographs of the phase morphology were observed at room temperature by OLYMPUS BH-2 type phase contrast microscopy (PCM) with a CCD and stored as video images. The time evolution of phase separation in the blend films was traced.

2.4. Atomic force microscopy

The surface morphologies of the blend films were also investigated with a Digital Instruments Multimode Nanoscope III AFM. Tapping mode AFM imaging was performed in air at room temperature. The AFM cantilever used was microfabricated from silicon and its spring constant and resonant frequency is 17.5 N m^{-1} and 210 kHz, respectively. Image analysis was performed using commercial DI software.

3. Results and discussion

3.1. Phase morphology

The phase morphology images of PMMA/HBP (80/20) blend samples annealed for different times are shown in Fig. 2. An aggregate appeared and grew bigger and brighter in the blend film with increasing the annealing time. In Fig. 2(a), a characteristic phase-separated morphology formed after spin-coating because of the thermodynamic incompatibility. PMMA and HBP domains appear dark and bright, respectively. The bright basic HBP granules dispersed in the dark PMMA continuous phase. After annealed at 230 °C for 2 min, it was observed that the HBP granules aggregated and formed a bright core as shown in Fig. 2(b). In Fig. 2(c), the bright core grew gradually to a special structure with a round section viewed from top after annealed for 4 min. We measured the diameter of the core structure and the thickness of the film, and the

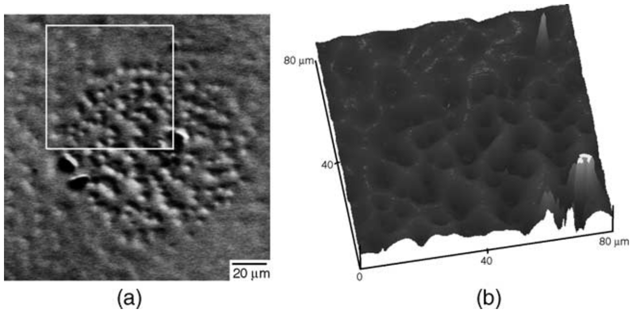
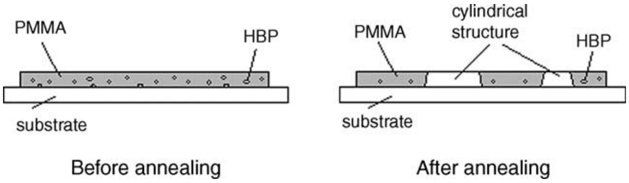


Fig. 3. (a) OM image of a cylindrical structure in a PMMA/HBP(80/20) blend film on glass substrate annealed at 230 °C. (b) AFM tapping mode height image of the white square area shown in (a).



Scheme 1. Scheme of the formation of the cylindrical structure.

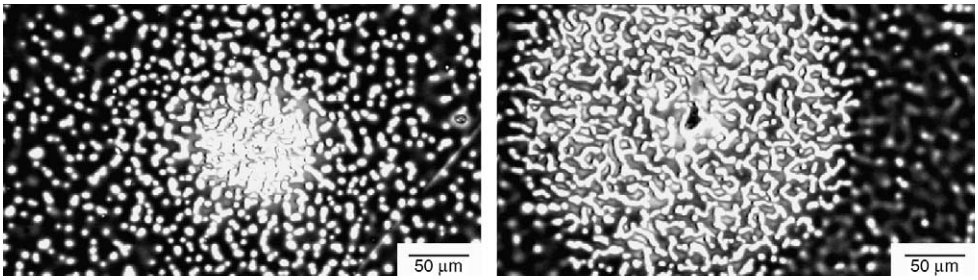


Fig. 4. The cylindrical structures in different locations of a PMMA/HBP(80/20) blend film on glass substrate annealed at 230 °C.

thickness of the film for Fig. 2 through Fig. 5 is 456 nm. It was found that the diameter of the structure was about 100 times larger than the thickness of the film. So the special structure should be a cylindrical structure. Further investigation on the surface morphology of the film was carried out with AFM. Fig. 3 shows the optical microscope image and AFM height image of a special structure in the film, respectively. The spatial representation of the square shown in Fig. 3(a) indicated that the height of the structure is higher than that of other locations. So it could be concluded that the special structure is a cylinder. It seems that the density of the HBP granules inside the cylinder is larger than the outside. At 10 min, a larger and brighter cylinder appeared as shown in Fig. 2(d), it implies that the ratio of HBP inside the cylinder continuously became larger too. The HBP granules collided and developed to strip-shaped both inside and outside of the cylinder. The diameter had a slightly growth after annealed for 25 min. The ratio of HBP inside the cylinder and the brightness of the cylinder increased slowly. For both the bright HBP phase and the dark PMMA phase, no further obvious changes could be observed for longer annealing time. When the weight percents of PMMA in the blend films varied in the range of during 70–90%, the morphologies of phase separation were similar.

The structure of the HBP molecule used here consists of several benzene rings and the peripheral carboxyl groups have an asymmetrical distribution. By the arena–arena interaction [37], some HBP molecules could aggregate to a HBP granule with terminal carboxyl acid groups. As reported by Whitby et al. [38], carboxyl groups have strong interactions with the glass substrate. After spin-coating, HBP are scattered uniformly in the film. It can be considered that the basic HBP granules on or very close to the glass substrate are possibly ‘fixed’ on the substrate and become ‘cores’ because of the enhanced interfacial interaction between the HBP in the blends and the glass substrate. When the annealing temperature is above the glass transition temperatures of both components of the blend, the HBP granules unfixed on the substrate can move freely while the fixed HBP granules can not (as shown in Scheme 1). Because HBP and PMMA are immiscible, the HBP granules will move and diffuse each other to aggregate to minimize the total surface and interface energy in the blend system. If the HBP granules collide with the fixed core, the HBP granules will no more move and are around the fixed core. With the evolution of the collision between granules and core, the core will gradually grow and become a sphere. Due to the confinements of the substrate and the thickness of the film, a cylindrical but not a sphere structure formed. Since, the carboxyl groups exclude each other, the HBP granules totally covered with carboxyl groups are not able to aggregate any more. So the cylinder doesnot comprise a pure HBP phase, but the bright HBP granules with denser density than elsewhere.

It was found that the diameters of the cylindrical structures in different locations of a polymer blend film varied from 40 to 400 µm as shown in Fig. 4. As mentioned above, either the basic HBP granule on or near the glass substrate is possible to become the core fixed on the substrate. However, time is needed that the HBP granules in the vicinity of the substrate move a certain short distance to be fixed by the substrate. The time of the formation of the cores in different locations is diverse, so different cylinders have varied diameters. In Fig. 5, it was also observed that two close small cylinders grew and collided to become a larger elliptic cylinder with two cores. If two cores were closer after spin-coating, the two cylinders would grow and collide to aggregate into a larger cylinder.

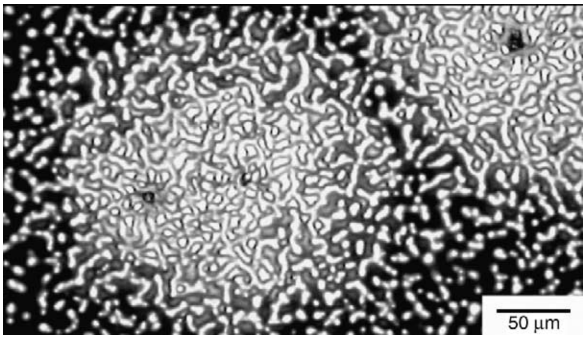


Fig. 5. The elliptic cylinder with two cores observed in a PMMA/HBP(80/20) blend film on glass substrate annealed at 230 °C.

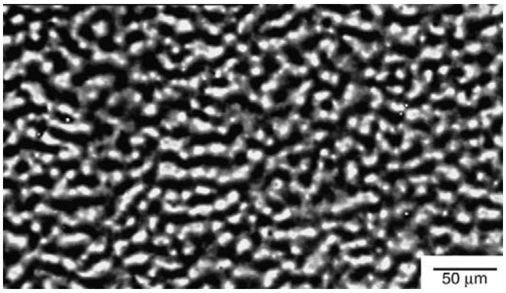


Fig. 6. Micrograph of the phase morphology of a PMMA/HBP(60/40) blend film on glass substrate annealed at 230 °C. The film thickness is 467 nm.

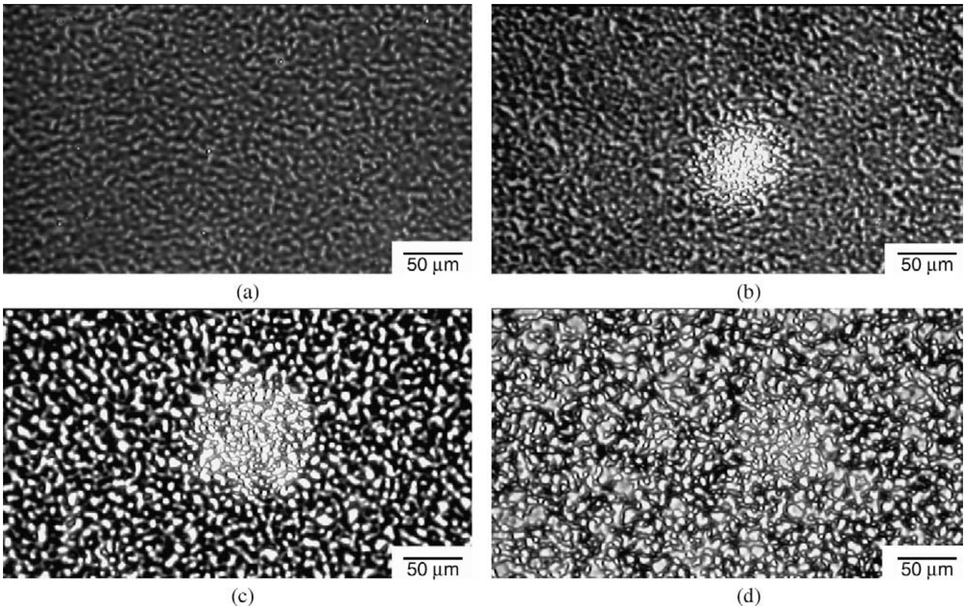


Fig. 7. Micrographs of the phase morphologies of PMMA/HBP(80/20) blend films with different thicknesses on glass substrate annealed at 230 °C after 10 min. The film thickness is (a) 150 nm, (b) 220 nm, (c) 500 nm, (d) 630 nm separately.

This is why the cylinders with different diameters could be observed in the same film.

The cylinder structure only formed at a low HBP percent in our experiments. It would become a bicontinuous structure when the weight percent of HBP increased to 40% as shown in Fig. 6. The number of both the cores and the HBP granules in 60/40 is larger than that in 70/30 for the blend films with the same thickness; the grown cylinders are so close that they easily collide each other to become a bicontinuous structure.

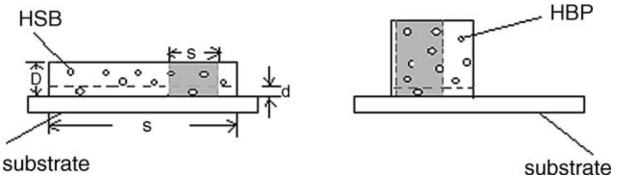
3.2. Critical film thickness

To the films with a fixed blend ratio, if the thickness of the film is thinner, the HBP granules should tend to be fixed on the substrates as cores. The thinner the film thickness, the more the fixed HBP granules are. If the thickness of the film is thin enough just to be equal size with the HBP granule, most of the HBP granules should be fixed onto the substrate. The phase morphology evolution should proceed very slowly in this case. Fig. 7 shows micrographs of the phase morphologies of 80/20 blend films with different thicknesses on glass substrate annealed at 230 °C after 10 min. No cylindrical structure could be observed in the thinner film as shown in Fig. 7(a). With increasing the film thickness, the cylindrical structure formed and became larger as shown in Fig. 7(b) and (c). When the film thickness is over 630 nm, the agglomerates appeared together with the cylinders everywhere in the film, some of them were as large as the cylinder so the boundary of the cylindrical structure is blurred. Fig. 7(d) shows a continuous structure of the agglomerates and the cylinders. Based on the results, it is concluded that the cylindrical structure only occurs in a certain film thickness range. In other words, there is a critical film thickness.

In order to gain insight into the presence of the critical film thickness, a model in Scheme 2 is put forward. To assume a blend solution drop is put onto the substrate at the beginning of the spin-coating process, the area S and the thickness D of the films spin-coated from a unit volume solution are in inverse ratio. When the component ratio is fixed, the number of total HBP granules N in a unit volume is constant. The granules placed in a very thin layer with the thickness d in the film can completely move to the substrate to become cores after annealing. The area of the field of vision of PCM (gray section shown in Scheme 2) is a constant s for a fixed enlargement. Now the number of the virgin cores after spin-coating in the field of vision n can be calculated by following equation:

$$n \approx \frac{ds}{DS} \times N \tag{1}$$

So, it can be concluded that n is almost the same for films with different D for a fixed volume. The number of HBP granules in the column with cross section of field of vision n' can be



Scheme 2. Scheme of films with different film thicknesses. The gray section is the field of vision of PCM.

Table 1
The critical film thicknesses of films with different component ratios

Component ratios (PMMA/HBP)	90/10	80/20	70/30
The critical film thickness d_c (nm)	245	204	110

calculated by this equation:

$$n\prime = \frac{s}{S} \times N \tag{2}$$

Obviously n' and D are in direct ratio for a fixed volume. As mentioned above, the HBP granules in the super-thin film are almost fixed on the substrates. In this case, $d \approx D$, $n \approx n'$. The phase morphology evolution proceeds very slowly. When the film thickness increases to a critical film thickness d_c, n' is several times larger than n, after annealing the HBP granules that could move freely aggregate toward the cores. So until the thickness reaches d_c the cylindrical structure can be observed.

The critical thicknesses of the films were obtained for different component ratios. The critical thicknesses according to the 90/10, 80/20, 70/30 films are listed in Table 1. The d_c decreases with increasing the HBP weight percent. We assume the number of the total HBP granules in the 90/10 blend film is $N_{90/10}$, and the number of the total HBP granules in the 80/20 blend film is $N_{80/20}$. $N_{80/20}$ is larger than $N_{90/10}$. To the 90/10 and 80/20 blend films with the same thickness, the numbers of the HBP granules that could freely move are $(D-d)sN_{90/10}/(DS)$ and $(D-d)sN_{80/20}/(DS)$ separately. When the film thickness equals to the d_c of 90/10 film, $(d_{90/10lc}-d)sN_{80/20}/(d_{90/10lc}S)$ is larger than $(d_{90/10lc}-d)sN_{90/10}/(d_{90/10lc}S)$. In the 90/10 film, few HBP granules can move, so the cylindrical structure is not able to form. But in the 80/20 film, the HBP granules could still move and aggregate to form a cylinder. So the d_c of the 80/20 film is smaller than that of the 90/10 film. In summary, the critical film thickness d_c decreases with the increase of HBP weight percent.

4. Conclusion

Spin-coating a film of strongly immiscible polymers PMMA/HBP from a common solvent yields a well-defined cylindrical structure. We contribute the formation of the structure to three fundamental factors: (a) the preferential adsorption of HBP to the glass substrate; (b) the characteristic shape and terminal groups of HBP; (c) the geometrical confinement of the film. Also the critical film thickness of the cylindrical structure formation is detected. We find that there is a transition in the critical thickness as the HBP weight percent is varied. A simple model is presented to reveal the formation mechanism of the cylindrical structure and give a reasonable explanation of the dependence of the critical film thickness d_c on the blend film composition ratios.

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