

Morphology of polystyrene/poly(dimethyl siloxane) blends compatibilized with star polymers containing a γ -cyclodextrin core and polystyrene arms

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ABSTRACT

A star polymer with a γ -CD core and PS arms is used to compatibilize blends of the immiscible polymers PS and PDMS. The mechanism of compatibilization is threading of the CD core by PDMS and subsequent solubilization in the PS matrix facilitated by the star arms. Spun-cast films of this blend are examined with optical microscopy, scanning electron microscopy and atomic force microscopy. Blends without CD-star exhibit large-scale phase separation, whereas those containing CD-star exhibit very homogeneous morphologies in the optical microscope and nanometer-sized phase domains in the AFM. The effect of PDMS molecular weight on the blend morphology is insignificant. The morphology of the compatibilized films does not change significantly after annealing at 125 °C for 3 days, indicating that the CD-star polymer effectively stabilizes these blends at temperatures where both polymers are mobile and could otherwise undergo large-scale phase separation. The degree of compatibilization in these blends is correlated with the molar ratio of PDMS repeat units to CD-star molecules.

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1. Introduction

Blending of bulk polymers is a method used to engineer a polymeric material with a desirable combination of properties from the homopolymer components. Chemically dissimilar polymers typically have a positive enthalpy of mixing and a negligible entropy of mixing, therefore they are usually immiscible. In the particular case of polystyrene/poly(dimethyl siloxane) (PS/PDMS) blends, the phase diagram reported by Nose [1] shows a two-phase morphology even when heating to 200 °C, for PS molecular weights of 1400–230,000 g/mol and a PDMS molecular weight of 600 g/mol. In addition, stability problems arise with migration of the PDMS to the surface as well as non-uniform phase dispersion in the PS matrix [2]. Potential applications for PS/PDMS blends include hydrophobic surfaces, membranes [3], and tribology [4].

Improvements in the mixing and stabilization of incompatible blends are typically accomplished in one of two ways [5]. First, reactive compatibilization can be used to physically trap the blended polymer into a networked microstructure by crosslinking the components to create an interpenetrating polymer network. Second, a compatibilizer such as a block copolymer consisting of

blocks chemically identical to the homopolymers in the blend can be added to enhance mixing. The compatibilizer resides at the interface between the two phases and lowers the interfacial energy. This significantly reduces the phase domain size and achieves more intimate blending. The use of PS/PDMS block copolymers as compatibilizers for PS/PDMS blends has been reported [6].

In this paper we report a novel type of compatibilizer for polymer blends, and demonstrate its effectiveness for PS/PDMS blends. This compatibilizer is a star polymer consisting of a γ -cyclodextrin core and PS arms (CD-star). Cyclodextrins are cyclic starch molecules with a truncated cone-like structure and an empty, hydrophobic central cavity. A wide variety of polymers and small molecules can thread into this cavity, thus forming an inclusion complex [7,8]. When CD-star is added to an immiscible polymer blend such as PS/PDMS, the CD-star arms provide solubility with the PS matrix, while PDMS threads into the CD core. The threading process effectively "handcuffs" and disperses PDMS into PS, creating a compatibilized blend.

CD-star compatibilizers have some advantages over conventional block copolymer compatibilizers. Many different polymers are capable of threading the CD core, which means that the same CD-star molecule could be used to compatibilize several different A/B polymer blends in which polymer B is varied. Furthermore, many studies have shown that the diameter of the CD cavity restricts inclusion complex formation to polymers that can fit into the cavity [9]. Selection of α -, β - or γ -CD (which have different

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Table 1

Composition of blends shown in Figs. 2 and 3 containing 1 wt% CD-core.

PDMS content and mol. wt.	CD-star (mg)	PDMS (mg)	PS (mg)	PDMS repeat units /CD-star (mol/mol)	CD-stars/PDMS chain (mol/mol)	Morphology observed
PDMS62						
1 wt%	40.3	5	454.7	17.5	48.3	compatibilized
5 wt%	40.3	25	434.7	87.5	9.7	compatibilized
10 wt%	40.3	50	409.7	175	4.8	grainy
20 wt%	40.3	100	359.7	350	2.4	large domains
PDMS308						
1 wt%	40.3	5	454.7	17.5	237	compatibilized
5 wt%	40.3	25	434.7	87.5	47.5	compatibilized
10 wt%	40.3	50	409.7	175	23.7	grainy
20 wt%	40.3	100	359.7	350	11.9	large domains

cavity diameters) as the core of the star polymer allows the compatibilizer to be tailored for selective threading of the desired polymers. To date, CD-star polymers have not been considered as compatibilizers for polymer blends but have been used by other researchers to create uniform porous films [10] or as crosslinkers to form interpenetrating polymer networks [11].

In a previous paper, we reported the synthesis of a series of γ -CD-star polymers with PS arms and showed that they were effective as compatibilizers for immiscible solutions of PS and PDMS in chloroform [12]. In this paper, the morphology of PS/PDMS films spun-cast from these compatibilized solutions is explored to assess the effectiveness of CD-star polymers as compatibilizers in polymer blends.

2. Experimental

2.1. Materials

ACS grade chloroform was purchased from Fisher Scientific and was used without further purification. Polystyrene homopolymer was purchased from Aldrich and was found to have a molecular weight of 325,000 g/mol and a polydispersity index (PDI) of 2.95 via gel permeation chromatography (GPC). Both poly(dimethyl siloxane) homopolymers used in this study were purchased from Gelest, Inc. and have PDIs between 2 and 3 and molecular weights of 62,700 and 308,000 g/mol. These are designated as PDMS62 and PDMS308, respectively.

2.2. Synthesis of γ -CD-star polymers

Synthesis of star polymers containing a γ -cyclodextrin core and PS arms was reported in a previous paper [12]. The arms were

grown from initiator sites on the CD-core using atom transfer radical polymerization, which produced well-controlled mono-disperse arm lengths. The CD-star used in this work has an average of 12 PS arms each containing 6 PS repeat units. ^1H NMR analysis showed that the 12 modified hydroxyl groups include 8 secondary and 4 primary hydroxyls [12]. The primary hydroxyls are located on the "top" (smaller diameter end) of the CD truncated cone, while the secondary hydroxyls are located on the "bottom" (larger diameter end) of the CD cone. Thus, it is reasonable to assume that threading of the guest polymer will occur predominantly from the top of the CD cone since fewer arms are present on that side. ^1H NMR was also used to determine the number average molecular weight of the CD-star, which was found to be 10,460 g/mol. GPC analysis showed that the CD-star is monodisperse with a PDI = 1.1, which is typical for ATRP reactions. The ^1H NMR molecular weight is considered more reliable than the GPC molecular weight in this case since the GPC column is calibrated with linear polymers rather than star polymers.

2.3. Preparation of spun-cast films

Precursor solutions of PS and PDMS with and without CD-star were prepared at a total solids concentration of 10 g/dL in chloroform. Tables 1 and 2 list the compositions of these solutions, where the percentages are based on the total amount of solids. Consequently, these are also the compositions of the resulting solid films. It should be noted that whenever the sample composition changes, PS is removed to keep the total mass of solids constant at 500 mg. The amount of CD-star in the blends is specified as "wt% CD-core", which excludes the mass of the PS arms. All solutions were turbid immediately after preparation, but became clear (compatibilized) after stirring at room temperature for 16 days, as shown in Fig. 1.

Table 2

Composition of blends shown in Figs. 6 and 7 containing 5 or 10 wt% PDMS.

PDMS content and mol. wt.	CD-star (wt% CD-core)	CD-star (mg)	PDMS (mg)	PS (mg)	PDMS repeat units /CD-star (mol/mol)	CD-stars/PDMS chain (mol/mol)	Morphology observed
5 wt% PDMS							
PDMS62	0.2	8.06	25	466.9	438	1.9	grainy
PDMS62	0.6	24.18	25	450.8	146	5.8	compatibilized
PDMS62	1.0	40.3	25	434.7	87.5	9.7	compatibilized
PDMS308	0.2	8.06	25	466.9	438	9.5	grainy
PDMS308	0.6	24.18	25	450.8	146	28.5	compatibilized
PDMS308	1.0	40.3	25	434.7	87.5	47.5	compatibilized
10 wt% PDMS							
PDMS62	0.2	8.06	50	441.9	875	1.0	large domains
PDMS62	0.6	24.18	50	425.8	292	2.9	grainy
PDMS62	1.0	40.3	50	409.7	175	4.8	grainy
PDMS308	0.2	8.06	50	441.9	875	4.7	large domains
PDMS308	0.6	24.18	50	425.8	292	14.2	grainy
PDMS308	1.0	40.3	50	409.7	175	23.7	grainy

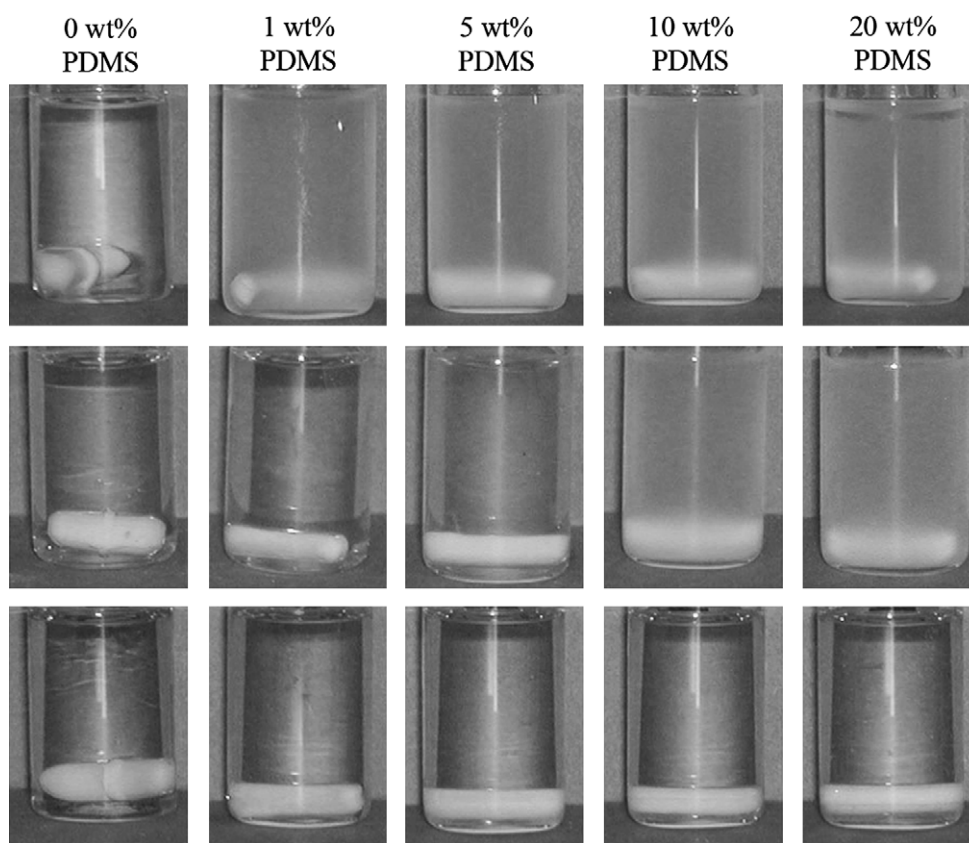


Fig. 1. Solutions of PS, PDMS and CD-star in chloroform stirred at room temperature for 1 h (top row), 6 days (middle row) and 16 days (bottom row). All solutions contain CD-star at 1 wt% CD-core. After 16 days the solutions become compatibilized as evidenced by solution clearing. White magnetic stirbars on vial bottoms can be used to judge solution clarity.

Solutions without CD-star remained turbid and did not clear under any conditions.

Boron-doped silicon wafers (4 in. diameter) with $\langle 100 \rangle$ orientation were purchased from WaferNet and cut into pieces

measuring approximately 1.5×1.5 cm using a diamond-tipped knife. The wafer pieces were subjected to intense UV irradiation for 30 min to break the Si–O–Si bonds on the surface, which was immediately followed by a series of 10-min solution treatments to

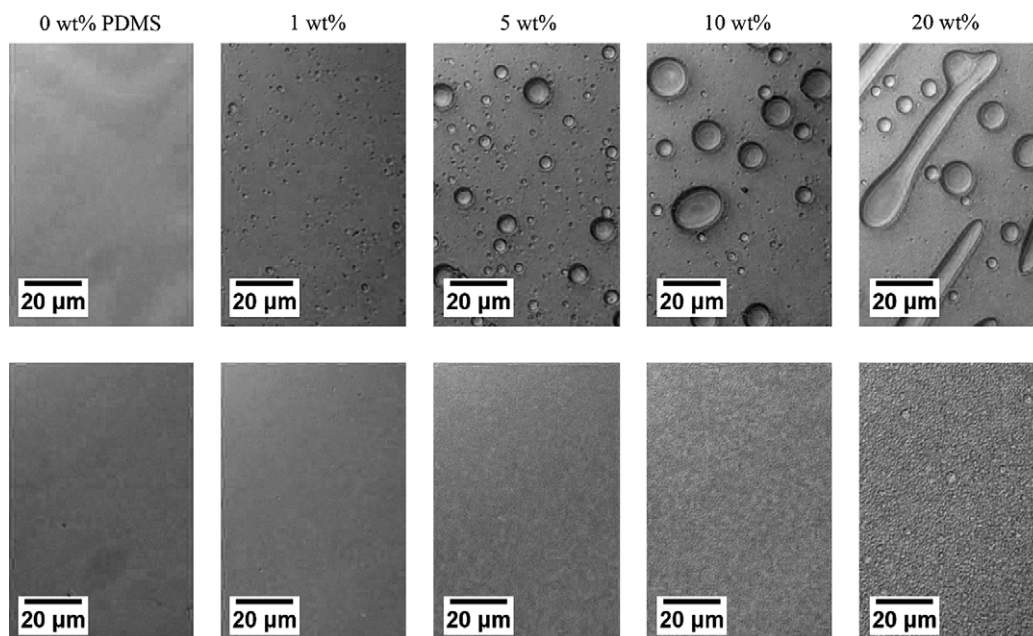


Fig. 2. Reflection optical micrographs of PS/PDMS62 spun-cast films with varying amounts of PDMS62. Top row: blends without CD-star. Bottom row: blends containing CD-star at 1 wt% CD-core.

hydrolyze the surface. The hydrolysis treatments included (i) deionized water, (ii) Baker-Clean® (JTB-111), (iii) deionized water, and (iv) isopropyl alcohol. Following the final solution treatment, all wafer pieces were dried under a nitrogen stream. The treated wafers had a very hydrophilic surface with a water contact angle that was essentially zero.

Spin-casting of the PS/PDMS/CD-star solutions onto the wafer pieces was conducted with a spin-coater under atmospheric conditions at 3000 rpm for 60 s. The spun-coated wafers were then dried overnight in a fume hood at room temperature followed by heat treatment at 60 °C for 3 h. Film thicknesses ranged from 1.5 to 1.8 μm , as measured by a profilometer.

2.4. Annealing procedure

Spun-cast films on silicon substrates were annealed in a vacuum oven at 125 °C for 3 days under a constant flow of dry nitrogen. The oven containing the samples was evacuated and backfilled 3 times with nitrogen before initiating the annealing experiments. After 3 days, the heat was terminated and the samples were allowed to cool to room temperature in the oven, while remaining under nitrogen. The annealing temperature is well above the glass transition temperature for PS (100 °C) and the melting point for PDMS (−40 °C).

2.5. Microscopic analysis

Optical microscopy was performed with an Olympus BH-2 microscope. Reflectance images of the spun-cast films on the silicon substrates were captured at 300 dpi by a ProgRes C10-plus CCD camera fitted onto the microscope.

Secondary electron images of the spun-cast films were obtained on a Hitachi S-3200N scanning electron microscope (SEM) operating at an accelerating voltage of 5 kV. The silicon wafer substrate was mounted on the aluminum sample stage with double-sided conductive carbon tape. The spun-cast films affixed to the sample

stage were then coated with a thin layer of Au/Pd alloy in a Denton Desk II sputter coater to reduce sample charging.

Atomic force microscope (AFM) images for spun-cast films on silicon substrates were collected with a Veeco Dimension 3000. These experiments were conducted in tapping mode with a resolution of 512×512 pixels. Vista Probe T300R-25 non-contact mode silicon AFM tips were used with a nominal resonance frequency of 300 kHz and a z-axis resolution of 15 pm.

3. Results and discussion

3.1. Morphological observations

Figs. 2 and 3 show optical micrographs of spun-cast films containing 0 or 1 wt% CD-core and varying amounts of PDMS62 or PDMS308. The compositions of these samples are reported in Table 1. Samples without CD-star are clearly phase separated and contain PDMS domains which increase in size and number with increasing PDMS content. The precursor solutions from which these films were spun-cast were cloudy and could not be clarified with extended stirring or heating. The phase separation evident in these films is therefore a reflection of the turbid state of the precursor solution. Conversely, samples containing CD-star at 1 wt% CD-core that were spun-cast from a clear solution are devoid of any large PDMS domains and are very homogeneous. Microscopic PDMS domains are just discernible in the samples containing CD-star only when the PDMS content reaches 10 wt%, lending a grainy appearance to these samples. The graininess slightly increases at 20 wt% PDMS, but no large-scale phase separation is observed. This homogeneous morphology is indicative of a compatibilized polymer blend in which the phases are mixed on a very fine scale. The PDMS molecular weight has no significant effect on the morphology of these films, therefore subsequent figures will contain representative micrographs for one PDMS molecular weight only.

Fig. 4 shows higher resolution SEM images of films with and without CD-star. Both samples contain 10 wt% PDMS308. Micrometer-size

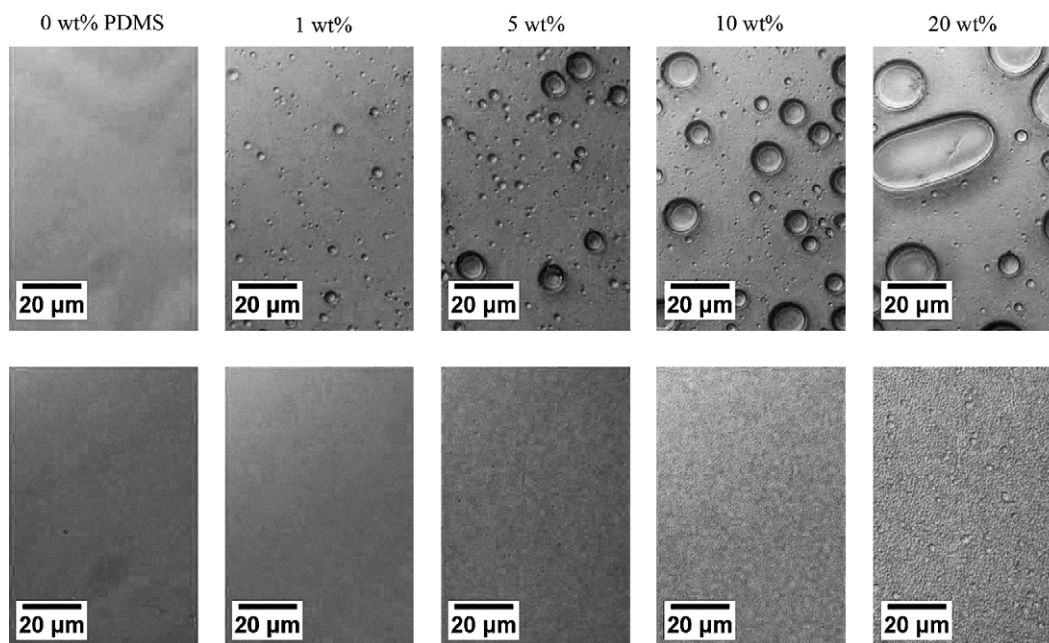


Fig. 3. Reflection optical micrographs of PS/PDMS308 spun-cast films with varying amounts of PDMS308. Top row: blends without CD-star. Bottom row: blends containing CD-star at 1 wt% CD-core.

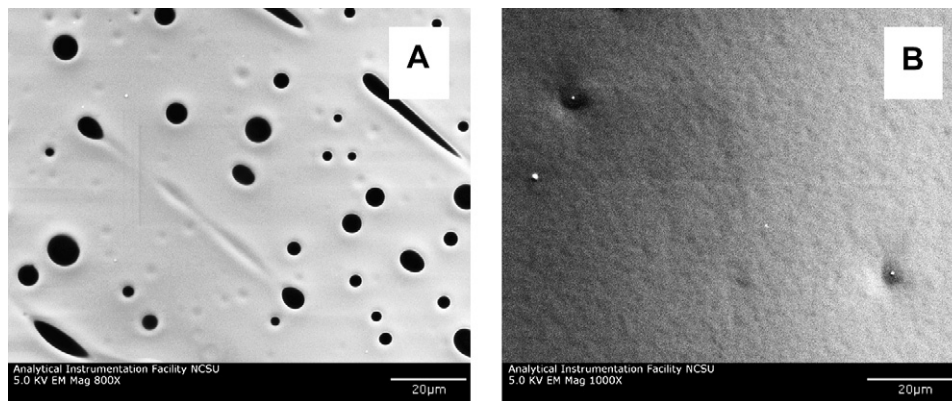


Fig. 4. Scanning electron micrographs of PS/PDMS308 spun-cast films containing 10 wt% PDMS308. Sample (A) contains no CD-star and sample (B) contains 1 wt% CD-core. The black regions in (A) are the PDMS domains.

PDMS domains (which appear black) are clearly visible in the sample without CD-star, while the sample with CD-star still looks homogeneous, featureless and well-compatible at this magnification.

To fully resolve the PDMS domains in the compatibilized films, it was necessary to use atomic force microscopy (AFM). Tapping-mode AFM images are displayed in Fig. 5 for films containing 1 wt% CD-core and varying amounts of PDMS308. The height images seem to show an increasing range of height values with increasing PDMS content, suggesting an increasing surface heterogeneity for these samples. The phase images are sharper and reveal a well-dispersed granular morphology with a domain size of 50 nm or less. The white areas in the phase images are the softer PDMS domains. The range of phase-lag values also seems to increase with increasing PDMS content, with the 20 wt% PDMS sample exhibiting the highest contrast in the phase images.

The compatibilized precursor solutions are thought to contain PDMS micelles [12,13]. The size of the PDMS domains in the phase images of Fig. 5 correspond well with the characteristic size of a micelle in solution. Apparently, the rapid evaporation of solvent which occurs during the spin-casting process provides little time for structural rearrangement, and the resulting blend morphology therefore reflects the structure present in the precursor solutions.

Fig. 6 presents representative optical micrographs of spun-cast films containing varying amounts of CD-star while the PDMS62 content remains constant at 5 or 10 wt%. The compositions of these samples and the corresponding PDMS308 samples are reported in Table 2. Again, the films without CD-star exhibit large-scale phase separation while those containing as little as 0.2 wt% CD-core appear to be well-compatible and homogeneous. In general, the samples containing 10 wt% PDMS exhibit a coarser morphology than the 5 wt% PDMS samples. The sample containing 0.2 wt% CD-core and 10 wt% PDMS contains micron-sized PDMS domains, which suggests incomplete compatibilization. However, the PDMS domain size is still much smaller for this sample compared to the corresponding one without CD-star. The large domains disappear completely when the CD-star content is increased to 0.6 or 1.0 wt% CD-core, and those samples exhibit a homogeneous, grainy appearance.

The images in Fig. 6 show a smooth progression in the degree of compatibilization as the amount of CD-star is increased, while Figs. 2 and 3 show a similar progression with decreasing PDMS content. This suggests that some borderline ratio of PDMS to CD-star must exist, below which the blends are compatibilized and above which graininess or larger-scale phase separation is observed. The molar ratio of PDMS repeat units to CD-star, as well as the molar ratio of CD-star to PDMS chains was calculated and compared with the visual observations noted in Figs. 2, 3 and 6. These results are listed in Tables 1 and 2. A designation of "compatibilized" in the last

column of these tables refers to a homogeneous morphology with no graininess at the resolution of the optical microscope. No correlation is noted between the observed morphology and the ratio of CD-star molecules to PDMS chains. However, a good correlation is found for the ratio of PDMS repeat units to CD-star molecules (hereafter the PDMS/star ratio). Blends with a PDMS/star ratio of 175 or higher consistently exhibit a grainy morphology or micron-sized PDMS domains. Blends with a PDMS/star ratio of 146 or lower have a more homogeneous, compatibilized morphology at the resolution of the optical microscope. This suggests that the borderline PDMS/star ratio for compatibilization in these systems is somewhere between these two values. Above this ratio, the blends contain insufficient CD-star and larger-scale phase separation occurs.

The observed morphologies do not correlate perfectly with the PDMS/star ratio. For example, the two blends with a PDMS/star ratio of 350 in Table 1 exhibit large PDMS domains, whereas the two blends with PDMS/star ratios of 438 in Table 2 should be less compatibilized, yet they exhibit a more homogeneous, grainy morphology with no large PDMS domains. This might be due to incomplete threading of the CD-star onto PDMS, leading to erroneous PDMS/star ratios. The PDMS/star ratios are based on the assumption that all of the CD-stars thread PDMS for all samples. Despite this inconsistency, it can be concluded that blends with a low PDMS/star ratio clearly exhibit a finer scale of mixing than those with high ratios.

3.2. Annealing studies

Annealing of a polymer blend can be used to assess the stability of the blend and to determine whether coarsening and further phase separation will occur. Annealing also relieves stresses incurred during preparation of the films and allows the blend to move toward equilibrium. Films having the same compositions as those in Figs. 2 and 3 (constant CD-star and variable PDMS content) were subjected to annealing for 3 days at 125 °C under a nitrogen atmosphere. This annealing temperature is well above the glass transition temperature for PS and the melting point of PDMS, so the blend components should be mobile and capable of structural rearrangement. For comparison, films without CD-star but having the same relative content of PS and PDMS were also annealed in parallel with those containing CD-star.

Optical micrographs for annealed films containing PDMS62 are displayed in Fig. 7. Very similar results were obtained for annealed films containing PDMS308. These can be compared with the unannealed films having the same compositions in Fig. 2. The annealed films containing CD-star exhibit a small amount of coarsening compared to the unannealed films, especially at 20 wt%

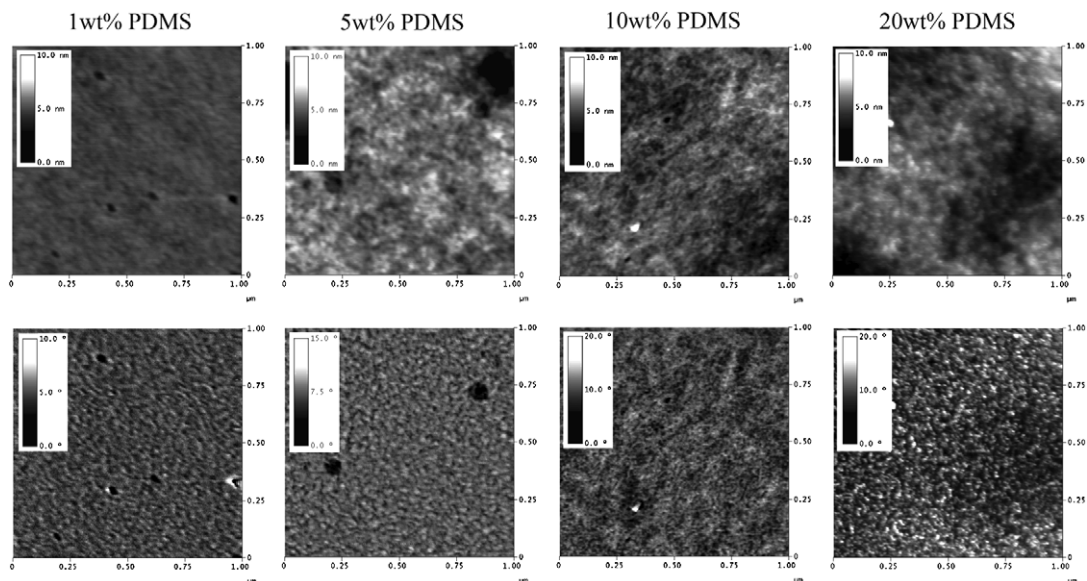


Fig. 5. Tapping-mode AFM images of PS/PDMS308 spun-cast films containing various amounts of PDMS308 and 1 wt% CD-core. The area scanned is $1 \times 1 \mu\text{m}$ in all cases. Top row: height images. Bottom row: phase images.

PDMS. This is somewhat expected since the samples with 20 wt% PDMS contain an insufficient amount of CD-star and are incompletely compatibilized. Samples with a PDMS content below 20 wt% exhibit no large-scale phase separation, indicating that the CD-star effectively stabilizes these blends at temperatures where both polymers are mobile and could otherwise undergo large-scale phase separation.

Minimal changes after annealing are also noted for the samples without CD-star in Fig. 7. However, some thickening of the PDMS domains in the vertical direction could be occurring in the annealed samples. Since these samples already exhibit large-scale phase separation, the driving force for additional coarsening is probably very low and little change in the morphology after annealing is expected.

Based on all of the above observations, the following general statements can be made regarding the phase behavior of the PS/PDMS/CD-star system. (1) At 0 wt% PDMS, the morphology consists of a single phase since CD-star is soluble in PS. (2) At 0 wt% CD-star, the morphology consists of two phases at all compositions and temperatures up to 200 °C, based on the results of Nose [1]. (3) At PDMS/star ratios less than 146, the morphology consists of nanodomains of PDMS in a PS matrix, stabilized by CD-star at the domain interface. (4) At PDMS/star ratios above 175, the morphology consists of nanodomains of PDMS stabilized by CD-star and larger domains which contain PDMS and little or no CD-star at the interface. The latter domains will grow in size with increasing amount of PDMS. We speculate that the larger domains observed for the CD-star containing samples in Figs. 2, 3, 6 and 7 are

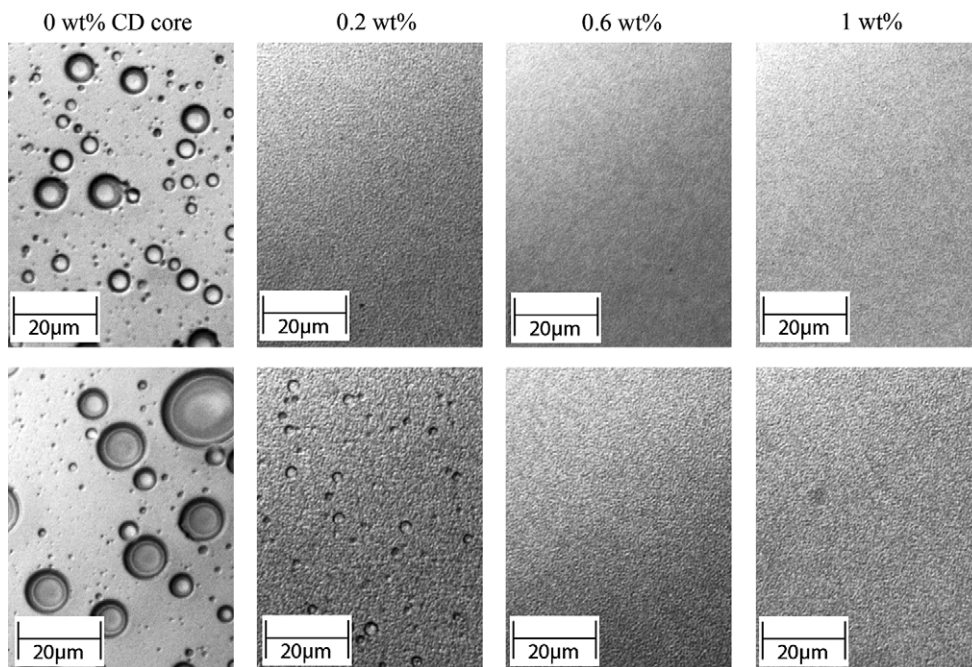


Fig. 6. Reflection optical micrographs of PS/PDMS62 spun-cast films containing various amounts of CD-star and 5 wt% PDMS (top row) or 10 wt% PDMS (bottom row).

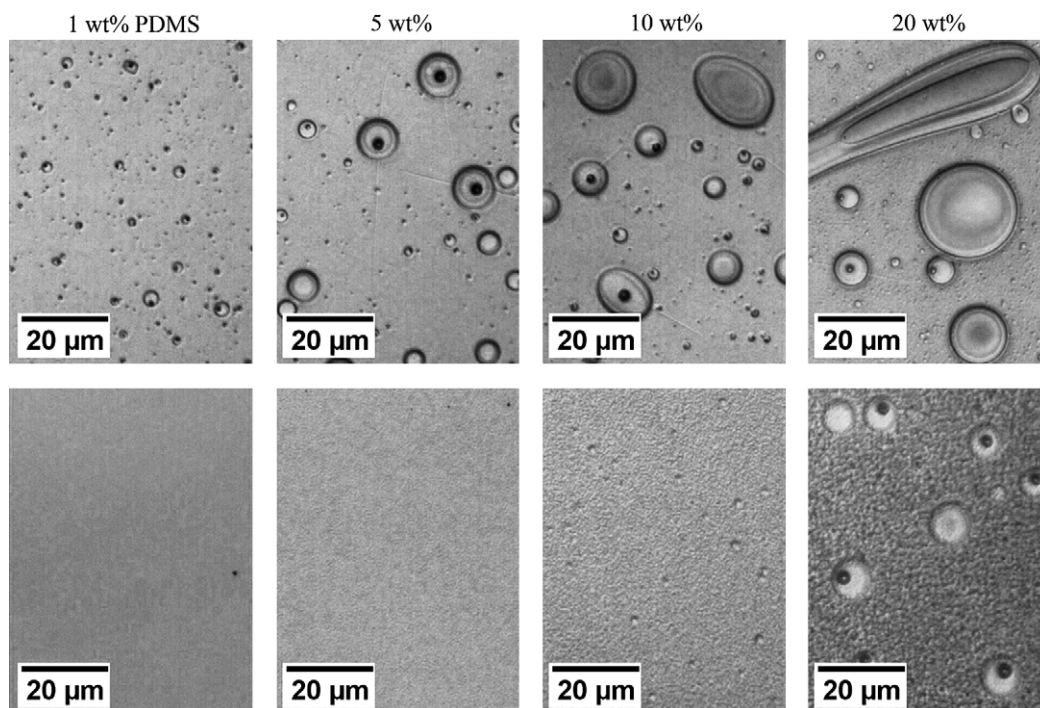


Fig. 7. Reflection optical micrographs of PS/PDMS62 spun-cast films containing various amounts of PDMS62 and annealed at 125 °C for 3 days. Top row: blends without CD-star. Bottom row: blends containing CD-star at 1 wt% CD-core.

of the latter type. (5) There is no evidence that the system will become completely miscible at some sufficiently high temperature. During the annealing study, two phases were observed for CD-star containing samples up to 125 °C.

4. Conclusions

It has been demonstrated that a star polymer with a γ -CD core and PS arms effectively compatibilizes blends of the immiscible polymers PS and PDMS. The mechanism of compatibilization is threading of the CD core by PDMS and subsequent solubilization in the PS matrix facilitated by the star arms. This novel type of compatibilizer could be advantageous compared to conventional block copolymer compatibilizers since many different polymers are capable of threading the CD core, which means that the same CD-star molecule could be used to compatibilize several different A/B polymer blends in which polymer B is varied. Selection of α -, β - or γ -CD (which have different cavity diameters) as the core of the CD-star also allows the compatibilizer to be tailored for selective threading of the desired polymers.

Optical microscopy reveals that spun-cast films of this blend without CD-star exhibit large-scale phase separation, whereas those containing CD-star exhibit very homogeneous morphologies. Phase separation in well-compatible films can only be observed with AFM, which shows that the PDMS domains are similar in size (50 nm or less) to PDMS micelles which form in solution prior to spin-casting. A high degree of compatibilization is achieved when the ratio of PDMS repeat units to CD-star molecules is at or below 146. At higher ratios, the films exhibit a grainy morphology or contain micron-sized PDMS domains. For PDMS308, this ratio corresponds to about 28 CD-star molecules per PDMS chain ($\sim 3\%$ coverage of the PDMS chain), assuming all of the CD-stars are threaded by PDMS. The PDMS molecular weight had no discernible effect on the morphology of these blends.

After annealing at 125 °C for 3 days, samples with a PDMS content below 20 wt% exhibit no significant change in morphology,

indicating that the CD-star effectively stabilizes these blends at temperatures where both polymers are mobile and could otherwise undergo large-scale phase separation. Samples containing 20 wt% PDMS are incompletely compatibilized and develop micron-sized PDMS phase domains after annealing.

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