Polymer 51 (2010) 6013–6020

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

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

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ARTICLE INFO

Article history:
Received 19 August 2010
Received in revised form
8 October 2010
Accepted 12 October 2010
Available online 20 October 2010

Keywords:
Blends
Compatibilization
γ-CD-star polymer

ABSTRACT

A star polymer with a γ-CD core and PS arms (CD-star) is used to partially compatibilize blends of the immiscible polymers polystyrene (PS) and poly(dimethylsiloxane) (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. Films cast from clear solutions in chloroform exhibit large wispy PDMS domains, indicating that some dethreading of CD-star and agglomeration of PDMS takes place during the slow process of solvent evaporation. However, DSC and DMA data show that partial compatibilization takes place, as evidenced by a shift in the PS and PDMS T_gs toward each other. The shift in PS T_g is greater when CD-star is present compared to samples without CD-star. PDMS also tends to leach out of the solution-cast films during solvent evaporation and post-processing of the films. The amount of retained PDMS is significantly increased when CD-star is present. The DMA data also show that PDMS has a lower molecular mobility when CD-star is present.

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 previous papers [7,8] we reported a novel type of compatibilizer for polymer blends, and demonstrated its ability to compatibilize PS/PDMS solutions and spun–cast thin films. 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 [9,10]. 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 the more 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

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doi:10.1016/j.polymer.2010.10.024

Table 1
Composition of blends initially containing 1 wt.% CD-core.

Initial PDMS content and molecular weight	CD-star (mg)	PDMS (mg)	PS (mg)
PDMS62			
1 wt.%	40.3	5	454.7
5 wt.%	40.3	25	434.7
10 wt.%	40.3	50	409.7
20 wt.%	40.3	100	359.7
PDMS308			
1 wt.%	40.3	5	454.7
5 wt.%	40.3	25	434.7
10 wt.%	40.3	50	409.7
20 wt.%	40.3	100	359.7

cavity restricts inclusion complex formation to polymers that can fit into the cavity [11]. Selection of α-, β- or γ-CD (which have different cavity diameters) as the core of the star polymer allows the compatibilizer to be tailored for selective threading of the desired polymers. Aside from our preliminary work [7,8], CD-star polymers have not been considered as compatibilizers for polymer blends but have been used by other researchers to create uniform porous films [12] or as crosslinkers to form interpenetrating polymer networks [13].

In this paper, thicker films of PS/PDMS blends are prepared by slow casting from solution. These films exhibit a higher degree of phase separation than the spun–cast films mentioned above. However, it is shown below that addition of CD-star to PS/PDMS films does produce changes in their thermal and mechanical properties and increases the retention of PDMS. This suggests that CD-star is still producing some degree of compatibilization in these samples.

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 weight average 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 weight average 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 [7]. The arms were grown from initiator sites on the CD core using atom transfer radical polymerization (ATRP) which afforded excellent control of the arm length. The CD-star used in this work has an average of 12 arms each containing 6 PS repeat units. GPC analysis confirmed that the CD-star had a narrow distribution of arm lengths with a PDI = 1.1. ^{1}H NMR analysis showed that the 12 modified hydroxyl groups include 8 secondary and 4 primary hydroxyls [7]. ^{1}H NMR was also used to determine the number average molecular weight of the CD-star, which was found to be 10,460 g/mol. The ^{1}H 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.

Table 2
Composition of blends initially containing 5 or 10 wt.% PDMS.

Initial PDMS content and molecular weight	CD-star (wt.% CD-core)	CD-star (mg)	PDMS (mg)	PS (mg)
5 wt.% PDMS				
PDMS62	0.2	8.06	25	466.9
PDMS62	0.6	24.2	25	450.8
PDMS62	1.0	40.3	25	434.7
PDMS308	0.2	8.1	25	466.9
PDMS308	0.6	24.2	25	450.8
PDMS308	1.0	40.3	25	434.7
10 wt.% PDMS				
PDMS62	0.2	8.1	50	441.9
PDMS62	0.6	24.2	50	425.8
PDMS62	1.0	40.3	50	409.7
PDMS308	0.2	8.1	50	441.9
PDMS308	0.6	24.2	50	425.8
PDMS308	1.0	40.3	50	409.7

2.3. Preparation of solution-cast films

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. Several series of solutions were prepared with PDMS contents ranging from 1 to 20 wt.% and CD-star contents ranging from 0.2 to 1.0 wt.% CD-core. The amount of CD-star in the blends is specified as “wt.% CD-core”, which excludes the mass of the PS arms. It should be noted that whenever the sample composition changes, PS is removed to keep the total mass of solids constant at 500 mg. All solutions were turbid immediately after preparation, but became clear (compatibilized) after stirring at room temperature for 16 days. Solutions without CD-star remained turbid and did not clear under any conditions.

Solution casting was performed in polytetrafluoroethylene (PTFE) boats to ensure that the films could be retrieved easily. A two-day controlled evaporation of the solutions was established by placing a glass dish over the films which was sealed along the edge by a paper towel to retard solvent evaporation and eliminate bubble formation. Following the controlled evaporation, the films were dried in a fume hood for up to two weeks, then were dried in a vacuum oven for 4 days at 60 °C.

The as-cast films were usually bowed. To flatten them for optical microscopy and dynamic mechanical testing, they were hot pressed for 5 min at 120 °C and 5000 psi between polyimide mold-release films and polished steel plates using a Carver press. The films were then removed from the heated platens and allowed to cool to room temperature. Finally, the samples were annealed at 90 °C for 14 days under vacuum to remove any residual stresses and remaining solvent. All films were processed in parallel to assure identical thermal histories. The final film thickness was approximately 200 μm.

During solution casting and thermal processing, it was noted that PDMS leached out of the films. PDMS residue was found in the PTFE casting boats and on the polyimide release film after the hot pressing process. Therefore, the PDMS content of the processed films is lower than what is listed in Tables 1 and 2. The retained PDMS content was determined using ^{1}H NMR as described in the Results and Discussion section.

2.4. Characterization

Transmission optical microscopy was performed with an Olympus BH-2 microscope. Images of the cast films were captured

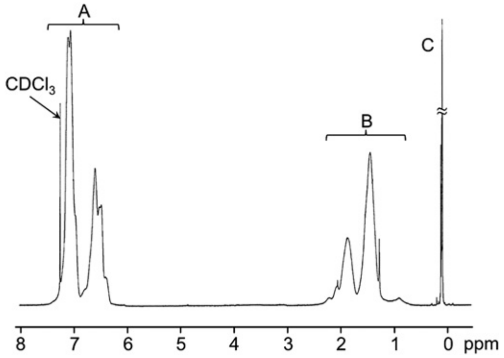

Fig. 1. A representative ^{1}H NMR spectrum for a PS/PDMS/CD-star film dissolved in CDCl$_3$. The three groups of peaks are due to (A) PS phenyl hydrogens, (B) PS backbone hydrogens and (C) PDMS hydrogens. The integrated intensity of group C was ratioed against the integrated intensity of group B to determine the amount of retained PDMS in the films.

at 300 dpi by a ProgRes C10-plus CCD camera fitted onto the microscope. The films were imaged after they were hot pressed, slow-cooled, then vacuum annealed at 90 °C for 14 days, as described above. This process, combined with the earlier prolonged solvent evaporation and 4-day, 60 °C vacuum annealing steps, ensures that an equilibrium morphology develops. ^{1}H NMR spectra were collected at room temperature on a Varian Gemini 300 MHz spectrometer equipped with a narrow bore magnet using 32 sampling repetitions. Differential scanning calorimetry was performed on a TA Instruments Q1000 calorimeter equipped with a liquid nitrogen cooling accessory. The cell constant was calibrated with sapphire from −140 to 300 °C and the temperature calibration was performed with indium having a melting point of 156.61 °C. Samples weighed approximately 10 mg, and they were scanned at 10 °C/min under a helium purge. To ensure a uniform thermal history and remove any sample-preparation artifacts, only the second DSC heating cycle is reported. Dynamic mechanical analysis was conducted on a TA Instruments DMA-600 in tension mode at a frequency of 1 Hz and a strain amplitude of 0.1%. Samples were initially equilibrated at −130 °C and were then scanned to 130 °C at a ramp rate of 2 °C/min.

3. Results and discussion

3.1. Amount of retained PDMS

As noted in the Experimental section, PDMS leaches out of the films during the solution casting and hot pressing operations. The amount of PDMS remaining in the films after processing was determined using ^{1}H NMR. Approximately 55 mg of each film was dissolved in 1 ml of CDCl$_3$ for ^{1}H NMR analysis. All films dissolved completely within 2 h, forming clear solutions. A typical spectrum is shown in Fig. 1. The integrated intensity of the PDMS proton peaks near 0 ppm was ratioed against the integrated intensity of the cluster of PS backbone proton peaks between 1 and 2 ppm. Comparison of this ratio with the expected PDMS/PS molar ratio from the initial film compositions shown in Tables 1 and 2 yielded the amount of PDMS remaining in the films.

These results are plotted in Figs. 2 and 3, which show the amount of retained PDMS as a function of initial PDMS content and wt.% CD core, respectively. The dashed lines represent the expected result if no PDMS is lost from the samples. Fig. 2 shows that samples with 1 wt.% CD core retain most of the PDMS until the initial PDMS content is about 10 wt.%. Beyond this value, the amount of retained PDMS levels off. For samples without CD-star, the amount of retained PDMS exhibits a gradual monotonic increase with increasing initial PDMS content, and is significantly lower. For example, samples initially containing 10 wt.% PDMS retain 8 wt.% when CD-star is present (at 1 wt.% CD core), whereas samples with the same initial amount of PDMS but no CD-star retain only 2 wt.%. This is evidence for the complexation of PDMS with CD-star, which retards the leaching of PDMS from the films. The amount of PDMS retained is independent of PDMS molecular weight for samples with and without CD-star.

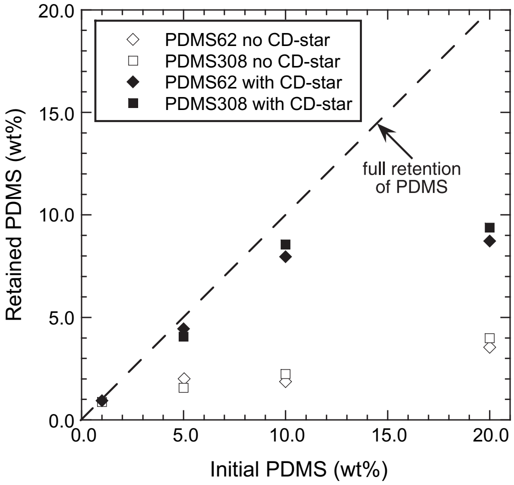

Fig. 2. Retained PDMS vs. initial PDMS content for films with and without CD-star. Films containing CD-star have a CD core concentration of 1.0 wt.%.

Fig. 3 shows the results for samples initially containing 5 or 10 wt.% PDMS and varying amounts of CD-star. The amount of retained PDMS initially increases as the amount of CD-star increases, but then it levels off at about 80% of the initial value and is again independent of PDMS molecular weight. The presence of plateaus in Fig. 3 suggests that a fixed ratio of CD-star molecules to PDMS repeat units exists, beyond which addition of more CD-star does not increase the amount of retained PDMS. With only four data points, the onset values for the plateaus are not clearly established, but appear to occur at 0.2 and 0.6 wt.% CD core for the 5% and 10% PDMS samples, respectively. These values correspond to one CD-star molecule for every 328 PDMS repeat units for the 10% PDMS samples, and one CD-star molecule for every 233 PDMS repeat units for the 5% PDMS samples, assuming all of the CD-star is

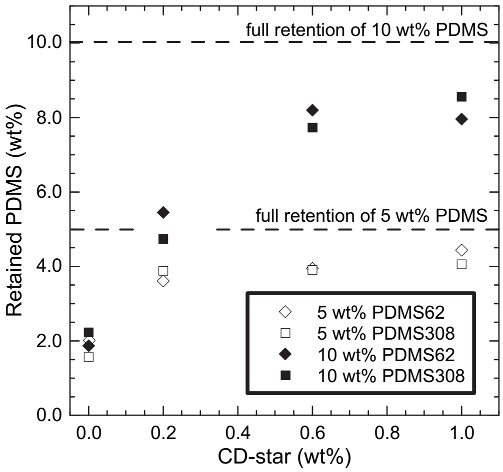

Fig. 3. Retained wt.% PDMS vs. wt.% CD-core for samples initially containing 5 and 10 wt.% PDMS62 or PDMS308.

threaded by PDMS. These numbers show that small amounts of CD-star threaded onto PDMS can significantly restrict the mobility of PDMS in PS, preventing most of the PDMS from leaching out of the blend. This lack of PDMS mobility is further verified in the DMA results below.

3.2. Morphology

Fig. 4 shows transmission optical micrographs of films containing 0 or 1.0 wt.% CD-core and varying initial amounts of PDMS308. These micrographs correspond to the samples used to collect the data in Fig. 2. Above each micrograph in Fig. 4 are pictures of these samples placed over the text “NC State”, which allows the relative transparency of the films to be compared. All films with PDMS displayed some cloudiness, while films containing only PS and CD-star were transparent (not shown). The micrographs clearly show a two-phase morphology, with the PDMS domains exhibiting a “wispy” appearance. Because the films are relatively thick (~200 μm), the micrographs contain superimposed images from focused and unfocused planes throughout the thickness of the sample. In general, the “wispy” appearance of the PDMS domains is more prevalent in samples containing CD-star, whereas some larger and more spherical domains are noted in samples without CD-star. Very similar results were obtained for the series of samples containing PDMS62.

The most significant difference between samples with and without CD-star lies in the overall transparency of these samples. The pictures above each micrograph show that the transparency of samples without CD-star decreases only slightly as the initial amount of PDMS in the samples increases. Conversely, the transparency of samples containing CD-star is much lower than the corresponding samples without CD-star, and the transparency decreases significantly with increasing initial PDMS content. These observations are consistent with the amount of PDMS retained in these samples. Samples without CD-star retain very little PDMS, and the amount retained increases very slowly with the initial PDMS content (see Fig. 2). There will be fewer PDMS domains in these samples to scatter light, resulting in a more transparent sample. The samples containing CD-star retain significantly higher amounts of PDMS, and the amount retained also increases significantly with increasing initial PDMS content. These samples have more PDMS domains, producing more light scattering and a lower transparency that decreases with increasing initial PDMS content.

Similar trends are noted for samples which start with the same initial PDMS content (5 wt.%) and contain varying amounts of CD-star, as shown in Fig. 5. These micrographs correspond to the samples used to collect the 5% PDMS data in Fig. 3. The same “wispy” morphology of the PDMS domains is noted for these samples, and no significant differences are apparent for samples containing PDMS62 and PDMS308. The transparency of the samples, as judged by the pictures above each micrograph, follows the same trend with retained PDMS noted in Fig. 4. Samples without CD-star retain the lowest amount of PDMS and are more transparent than those with CD-star. The amount of retained PDMS in the latter samples is nearly constant from 0.2 to 1.0 wt.% CD core (see Fig. 3), and the corresponding transparency of these samples does not change much.

The morphology and PDMS retention characteristics of these solution-cast films differs considerably from spun–cast films having the same composition, which were described in a previous paper [8]. In that paper, it was shown that spun–cast films containing CD-star have a very homogeneous, compatibilized morphology. The PDMS domains for samples having low PDMS repeat unit/CD-star ratios were not visible in the optical microscope, and atomic force microscopy was used to show that the PDMS domain size was on the order of 50 nm. At higher PDMS repeat unit/CD-star ratios, some PDMS domains were a few microns in size and were visible in the optical microscope. Spun–cast samples without CD-star had strikingly larger PDMS domains, which ranged up to 20 μm. Interestingly, no loss of PDMS was noted for the spun–cast samples.

The differences between solution-cast and spun–cast films can be attributed to the amount of time required to produce solid films from the precursor solutions using these two methods. The spin-

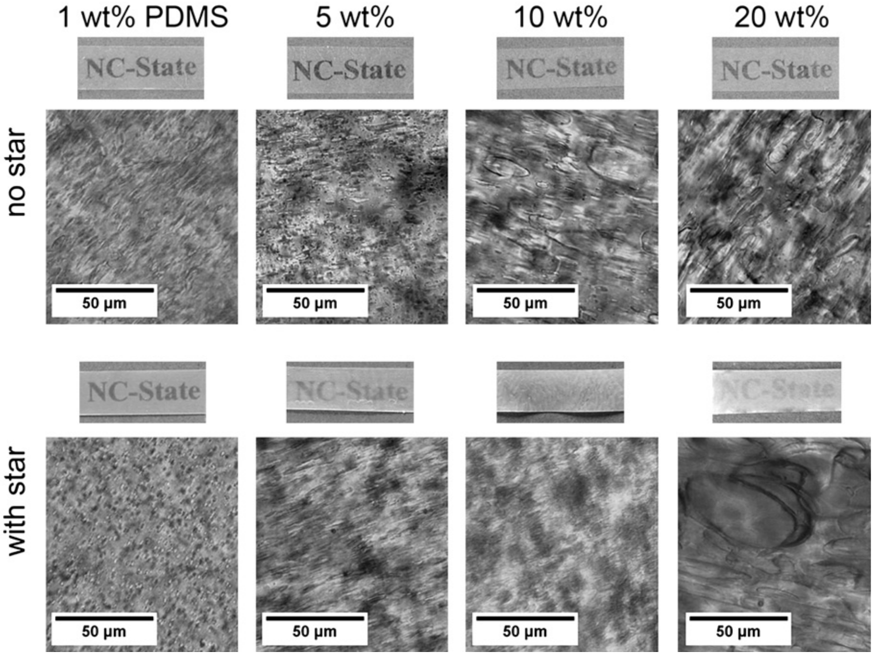

Fig. 4. Transmission optical micrographs for PS/PDMS308 films. CD-star concentration is 1.0 wt.% CD-core in samples with CD-star. Presented above each image are pictures of the films over the text “NC State” to illustrate film transparency.

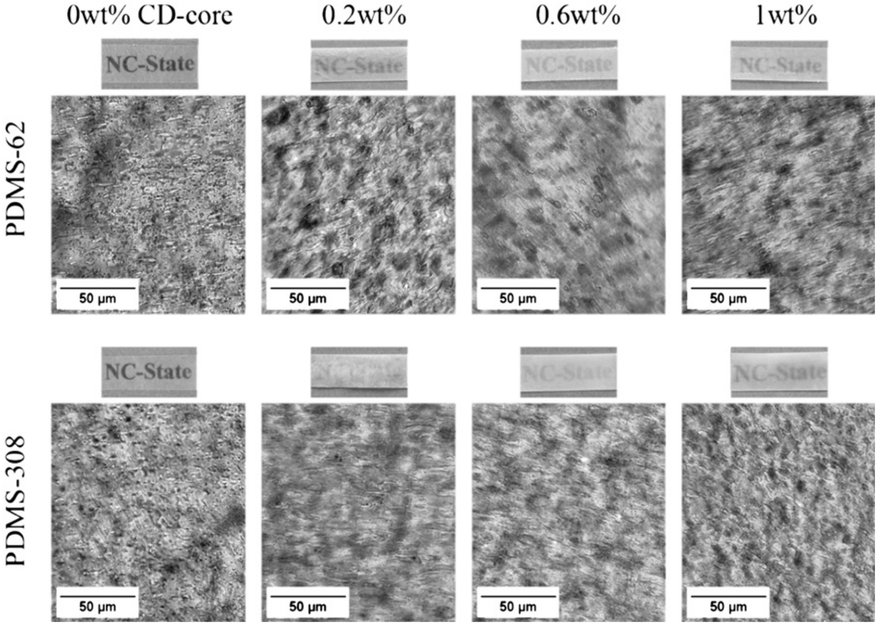

Fig. 5. Transmission optical micrographs for PS/PDMS films with 5.0 wt.% PDMS and varying amounts of CD-star. Presented above each image are pictures of the films over the text "NC State" to illustrate film transparency.

casting process produces thin films (1.5 μm) and requires only 1 min for solvent evaporation. These films are then annealed at 60 °C for 3 h while still attached to the silicon substrate. The rapid removal of solvent essentially prevents any significant agglomeration of the nano-sized PDMS micelles in solution, thus producing well-dispersed films. The PDMS is not simply kinetically trapped in these films, however, as extended annealing at 125 °C for two days under a nitrogen atmosphere does not induce any significant coarsening of the microstructure or noticeable loss of PDMS [8]. This temperature is well above the glass transition of polystyrene and the melting point of PDMS, so compatibilization of these two polymers by CD-star is robust for spun–cast films.

The situation is different for the solution-cast films, which are produced via slow solvent evaporation over a two-day period. As the solvent evaporates during this extended solidification time, the PDMS micelles in solution have a chance to agglomerate, which may be accompanied by some dethreading of PDMS from CD-star and leaching of the uncomplexed PDMS from the film. In addition, the solution-cast films are subjected to additional drying, hot pressing and annealing operations (as described in the Experimental section), all of which takes several weeks and provides additional opportunities for leaching of uncomplexed PDMS. This can account for the large PDMS domains and loss of PDMS from the solution-cast films. Even though CD-star does not completely prevent agglomeration of PDMS during the slow solution casting process, it still stabilizes PDMS in PS, as evidenced by the higher amount of PDMS retained in films containing CD-star.

3.3. Thermal behavior

DSC scans of the pure components comprising the solution cast films are displayed in Fig. 6. Both PDMS samples exhibit a T_g near −125 °C, cold crystallization near −85 °C, followed by melting near −40 °C. The DSC scan for CD-star is featureless except for the T_g associated with the PS arms at 90.5 °C. The homopolymer PS used in these samples exhibits a T_g of 102.5 °C. DSC scans for a series of films initially containing 10 wt.% PDMS308 and various amounts of CD-star are shown in Fig. 7. For each film, the amount of retained PDMS is also shown in this figure. The primary feature in these scans is the PS glass transition, which is reduced by a few degrees compared to pure PS. Occasionally a small endothermic peak is noted near −40 °C, associated with the melting of PDMS. The PDMS T_g is just visible for films having higher amounts of retained PDMS. Partial compatibilization of polymer blends is indicated when the glass transition temperatures of the components of the blend begin to shift toward each other [14,15]. Fully miscible blends are characterized by a single T_g that lies between the component T_gs [16].

In the PS/PDMS/CD-star samples studied here, only the PS T_g is reliably discernible in all the DSC scans. This value is plotted against CD-star content for several different samples in Fig. 8. The samples chosen for this plot had similar but not identical amounts of retained PDMS. The average amount of retained PDMS is shown in the legend for each set of samples, and the maximum variation about this average was ±0.4 wt.% for all sample sets. Samples containing only CD-star (no PDMS) exhibit a small reduction in T_g, due to the diluent effect of the low molecular weight PS arms on the CD-star which have a $T_g = 90.5$ °C. Samples containing CD-star and PDMS exhibit a larger T_g reduction which generally increases with increasing CD-star content, up to a maximum reduction of 7 °C.

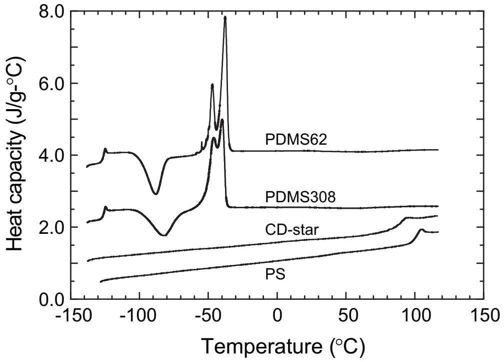

Fig. 6. DSC thermograms of the individual components making up the solution-cast films. The curves have been shifted vertically for clarity.

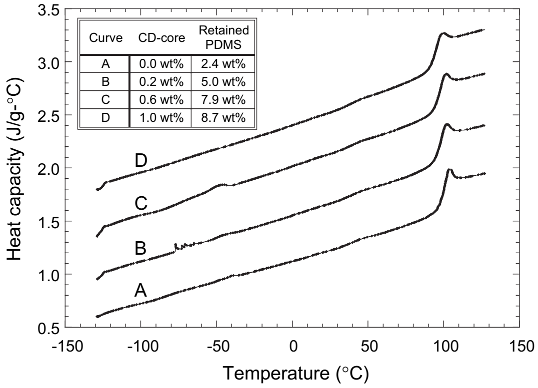

Fig. 7. DSC thermograms of a series of films initially containing 10 wt.% PDMS308 and various amounts of CD-star. The amount of retained PDMS308 for each film is listed in the table. The curves have been shifted vertically for clarity.

This trend is clear for all samples containing CD-star and PDMS. However, there are no clear trends in PS T_g with PDMS content or molecular weight. Addition of similar amounts of PDMS to PS without CD-star produces scattered T_g values which vary about the pure PS value by ±1–2 °C (data not shown). The larger shift in PS T_g toward the PDMS T_g that occurs when CD-star is present suggests that partial compatibilization of PS and PDMS takes place. This is a significant result, considering that PDMS is highly immiscible with PS and that small amounts of retained PDMS (4–8 wt.%) can influence the T_g of PS when partially compatibilized by CD-star.

3.4. Dynamic mechanical behavior

Dynamic mechanical analysis (DMA) is generally more sensitive than DSC for detecting weak thermal transitions in polymeric materials [17]. DMA was used here to identify changes in the PDMS T_g in the blended films containing CD-star, and also to explore any improvements in mechanical properties that may occur when PDMS is blended with PS and CD-star. No significant effects of PDMS molecular weight were observed in the DMA data, so only data for samples containing PDMS308 are presented.

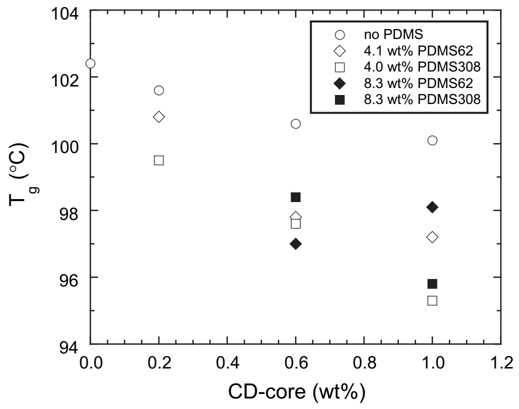

Fig. 8. Plot showing the variation in PS T_g with CD-star content for PS/PDMS/CD-star films. The average amount of retained PDMS is shown in the legend for each set of samples. The maximum variation in retained PDMS for all sample sets is ±0.4 wt.%.

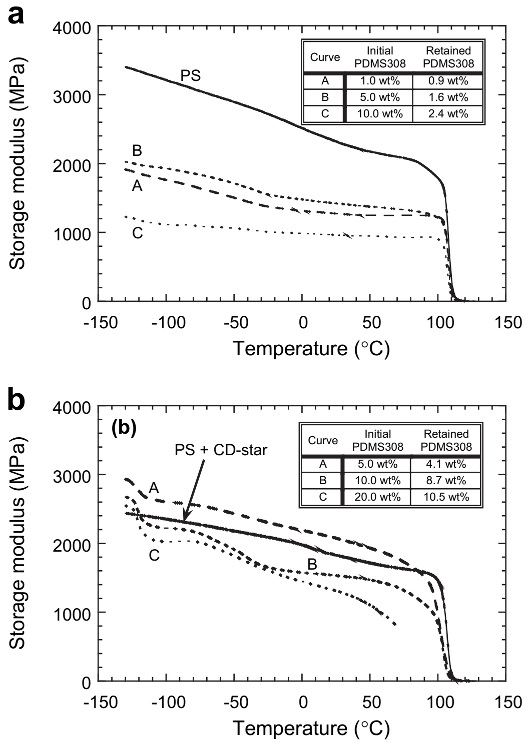

Fig. 9. Storage modulus vs. temperature for PS/PDMS308 films without (a) and with 1.0 wt.% CD-core (b). The solid lines represent samples with no PDMS308. For the remaining samples, the initial and retained amounts of PDMS308 are shown in the tables.

The storage modulus for films with various amounts of PDMS but no CD-star is plotted against temperature in Fig. 9a. This can be compared with Fig. 9b, which is a similar plot for a set of films containing CD-star. Both the initial and retained amounts of PDMS are shown for each sample in these figures. For all samples, the storage modulus drops abruptly as the PS T_g is approached around 100 °C. Additional drops in storage modulus can be seen around −123 and −40 °C for samples containing larger amounts of retained PDMS, which correspond, respectively, to the PDMS T_g and the melting of PDMS crystals. These changes can also be noted for the samples with smaller amounts of retained PDMS if plotted on an expanded scale. The PDMS T_g is well-defined for the samples in Fig. 9b, whereas this transition was weaker in DSC scans for samples containing similar amounts of retained PDMS (Fig. 7).

Addition of CD-star alone to pure PS causes the storage modulus to drop significantly at all temperatures up to the glass transition (compare the solid lines in Fig. 9a and b). This is due to the additional free volume and molecular mobility produced by the low molecular weight PS arms on CD-star, as noted earlier in the DSC PS T_g data (Fig. 8). The samples containing PDMS but no CD-star exhibit a significantly lower storage modulus compared to pure PS, as expected when blending a rubbery polymer with a glassy polymer. The decrease in modulus is significant considering that these samples contain only 0.9–2.4 wt.% PDMS308. Addition of CD-star to the PS/PDMS308 blends causes an increase in the storage modulus to levels comparable with the PS/CD-star sample, in spite of the fact that these samples retain much more PDMS308 than the samples without CD-star. A lower modulus would be expected for samples containing more PDMS. This indicates that the PDMS chains in these samples do not have as much molecular mobility as they do in samples without CD-star, which is further evidence for threading of PDMS into CD-star and partial compatibilization of the blend. The sample with 10.5 wt.% retained PDMS failed before the PS T_g was reached. Grip slippage and failure during the test was a common occurrence for other samples with similarly high levels of retained PDMS.

Fig. 10a and b display the corresponding loss modulus curves for the same samples as in Fig. 9a and 9. Addition of CD-star alone to

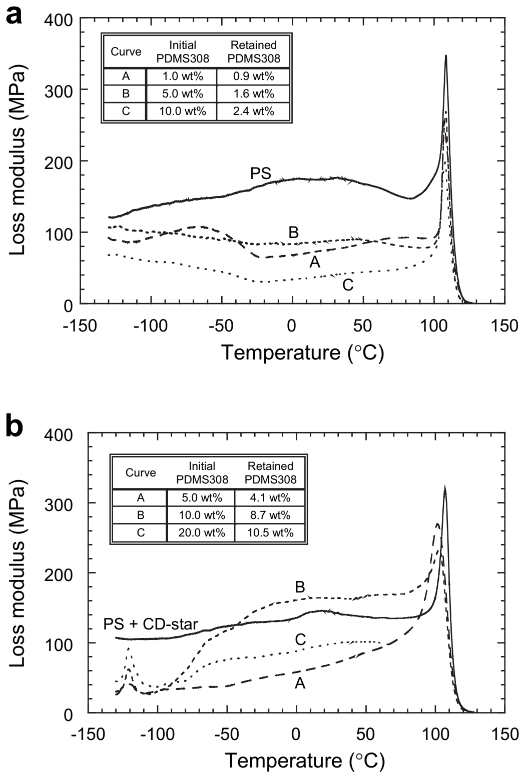

Fig. 10. Loss modulus vs. temperature for PS/PDMS308 films without (a) and with 1.0 wt.% CD-core (b). The solid lines represent samples with no PDMS308. For the remaining samples, the initial and retained amounts of PDMS308 are shown in the tables.

pure PS has very little effect on the loss modulus of PS (compare the solid lines in Fig. 10a and b). The broad peak from −50 to 50 °C in pure PS is reduced to a narrower peak centered around 20 °C for the sample containing CD-star. This peak may be due to the β-transition in PS [18]. The loss modulus for samples containing PDMS but no CD-star is reduced somewhat compared to pure PS. Addition of CD-star to PS/PDMS blends does not change the loss modulus much, even though these samples retain significantly more PDMS compared to those without CD-star. Samples with more PDMS should be more lossy. This is further evidence that the molecular mobility of PDMS is reduced when threaded into CD-star. For samples with CD-star, the loss modulus for blends containing PDMS remains below that for the sample containing only PS and CD-star, except for the sample with 8.7 wt.% retained PDMS, which slightly exceeds the loss modulus of PS/CD-star at temperatures above −40 °C.

Glass transition temperatures, as measured by the peak temperatures in the loss modulus curves in Fig. 10, are collected in Table 3. The PS T_g is affected very little by the addition of CD-star or PDMS alone, being reduced by about 1 °C. Conversely, addition of PDMS and CD-star to PS causes the PS T_g to drop by nearly 6 °C compared to pure PS. This level of reduction in PS T_g is consistent with the DSC data in Fig. 8. For the samples without CD-star and containing 1.6 or 2.4 wt.% retained PDMS (curves B and C in Fig. 10a), the PDMS T_g peak is weak but discernible around −123 °C. At these low levels of retained PDMS, the PDMS T_g was not visible in the DSC scans (data not shown). The PDMS T_g peak is more intense for the samples with CD-star (Fig. 10b), as these samples retain significantly more PDMS. The T_g for these samples is also shifted up slightly in temperature, ranging from −121.7 to −120.8 °C. While this shift is small, it was reproducible in all samples containing PDMS and CD-star, including samples prepared with PDMS62. The shift in PDMS T_g toward the PS value is another indication of partial compatibilization of PDMS with PS by CD-star.

Table 3
Glass transition temperatures for blend films from DMA (see Fig. 10).

Initial PDMS308 (wt.%)	Retained PDMS308 (wt.%)	CD-star (wt.% CD core)	PDMS T_g (°C)	PS T_g (°C)
0	0	0	–	108.4
1.0	0.9	0	n/a	107.1
5.0	1.6	0	−122.5	108.1
10.0	2.4	0	−123.2	107.9
0	0	1.0	–	107.1
5.0	4.1	1.0	−121.7	102.7
10.0	8.7	1.0	−120.8	102.8
20.0	10.5	1.0	−120.8	n/a

4. Conclusions

Solution-cast films of PS and PDMS are only partially compatibilized by the addition of CD-star. Transmission optical microscopy shows that these films contain relatively large phase-separated domains of PDMS having a “wispy” appearance. Although the precursor solutions of the film components in chloroform are clear and apparently fully compatibilized, some dethreading of PDMS from CD-star and agglomeration of the PDMS/CD-star complex apparently takes place during the slow process of solution casting. This is in stark contrast to the behavior of thin films which are rapidly spun–cast from the same precursor solutions [8]. The spun–cast films are very homogeneous and remain compatibilized even after annealing for two days at 125 °C. The PDMS molecular weight had very little effect on the morphology of the solution cast films or their thermal and dynamic mechanical properties.

The evidence for partial compatibilization of PS and PDMS by CD-star in solution-cast films comes from the following observations. (i) The PS and PDMS T_gs shift toward each other, as verified by DSC and DMA measurements. The shift in T_g is greater when CD-star is present compared to samples without CD-star. (ii) PDMS tends to leach out of the films during solution casting. When CD-star is present, a significantly larger amount of PDMS is retained in the films. (iii) Samples containing CD-star exhibit a higher storage modulus and a lower loss modulus than samples without CD-star, even though the amount of retained PDMS is higher when CD-star is present. This indicates that the molecular mobility of PDMS is diminished when it threads into CD-star and is physically handcuffed in the PS matrix.

Acknowledgements

The authors gratefully acknowledge financial support from N. C. State University and the National Textile Center, Grant #M06-NS02.

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