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Modification of the phase stability of polymer blends by fillers

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Abstract

We investigate the influence of filler particles on the phase stability of a model blend of polystyrene (PS) and polybutadiene (PB). The upper critical solution temperature cloud point curve of a PS:PB blend is "destabilized" (upward shift of cloud point temperature) by the addition of untreated fumed silica filler particles. Preliminary cloud point measurements on surface-functionalized fumed silica particles were also performed. A small downward shift of the cloud point temperature was observed by functionalizing the filler particles with grafted polystyrene chains, while grafting with a silane coupling agent resulted in a large apparent "stabilization" effect or a decrease of the cloud point temperature. (Further measurements on surface-functionalized filler particles over a range of polymer compositions are required to determine the filler concentration dependence of the shift of the blend critical temperature.) Surface treatments were selected to demonstrate that modifying the filler particle surface chemistry can alter the blend phase boundary. These phase boundary shifts have significance in commercial blends containing dispersions of filler particles. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Polymeric materials are rarely used for applications in their pure form. They are often mixed with additives that alter their processability, modulus, impact strength, appearance, conductivity, or flammability [1]. Moreover, tailoring of polymer bulk properties may be achieved by blending different polymers. However, the improved properties of polymer blend materials may be compromised over long time scales due to a general tendency towards demixing. The present paper focuses on how filler particles modify the phase stability of polymer blends and how the surface chemistry of the filler particles influences this effect. Controlling the phase boundary is of practical importance because the quench depth (distance in temperature into the two-phase region) is a determining factor governing the stability of these multiphase mixtures against macroscopic phase separation.

It is well known that block copolymer and solvent additives can shift the phase boundary of polymer blends and this idea is a common strategy for "compatibilizing" polymer blends [2–4]. The usual goal for forming these mixtures is to achieve greater miscibility and reduced interfacial tension so that dispersion of one polymer within another is accomplished more readily than without the additive. However, all additives do not improve blend miscibility and improved miscibility often comes at the expense of other bulk properties. Phenomenologically, it has been established that the phase boundary can shift either up or down depending on the interaction and geometrical structure of the additive [2–4]. This is also observed in magnetic phase transitions, where the sign of the critical temperature shift depends on the interaction of the surface spins relative to those in the bulk [5]. The applicability of the theory for molecular additives (e.g. solvent and copolymer additives in blends) to describe filler particle dispersions remains to be established.

Recently, Dudowicz et al. [6] investigated the case of block copolymers of varying mass ratio in polymer blends and found results providing quantitative insights into the shifts in phase behavior with molecular additives. The calculations of Dudowicz et al. can be specialized to the case of compact particle additives, modeling solvents of variable interaction with the fluid. These calculations give results very similar to those for magnetic phase transitions with impurities [5], and this problem can be exactly related in the limit of small molecule phase separation [7,8]. Model calculations for both blend and magnetic phase transitions indicate limits on the slope of the concentration dependence of the critical temperature that are discussed below.

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Shifts in the cloud point of polymer blend films in the presence of untreated and surface treated fillers have been observed previously by Nesterov et al. [9,10] This work indicated a change in the qualitative type of phase separation behavior from an upper critical solution type cloud point curve to a lower critical solution type cloud point curve. A companion paper on the same filled blend [9,10] claimed that even the *sign* of the phase boundary shift depended on the relative polymer composition and this effect was attributed to the interactions between the polymers and the filler particles [9,10]. Scherbakoff and Ishida noted the "improved compatibility" of an immiscible blend containing surface treated glass beads relative to the untreated beads using rheological methods [11]. However, the determination of the phase boundaries in these samples was not performed by Scherbakoff and Ishida. Since previous theoretical and experimental work also suggests that the differential interaction between the polymers in the mixture for the additive are important for understanding the sign and character of the phase boundary shift, we modify the surface chemistry of the particles to explore this effect.

In the present paper, we measure the cloud point curve of a low molecular weight polystyrene (PS) and polybutadiene (PB) model blend (PS:PB). The cloud point curve is also measured on a model blend containing fumed silica. Utilizing the same fumed silica, the surface of the filler particles was modified in two ways. One portion of fumed silica was treated by grafting PS chains onto the filler surface. A second portion of fumed silica was modified with a bromomethyldimethylchlorosilane (BMDMCS) coupling agent. These treated silicas have different surface energies than the untreated silica leading to different phase modifications of the PS:PB blends.

2. Experimental

The polymers utilized were PS ($M_w = 1800$ g/mol)[1] and PB ($M_w = 2800$ g/mol) purchased from Goodyear Tire and Rubber Co.[2] The PS contains a mass fraction of approximately 10% insoluble inorganic solids as received and was purified by dissolving the polymer in benzene and filtering through a PTFE filter. The resulting solution was freeze-dried to isolate the PS. The PB was used without further purification. The filler is a hydrophilic fumed silica (BET = 250 m^2/g) obtained from Dow Corning Corporation[2] and

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[1] According to ISO 31-8, The term Molecular Mass has been replaced by Relative Molecular Mass, symbol M_r. Thus, if this nomenclature and notation were to be followed, one would write, $M_{r,n}$, instead of the conventional M_w for the weight average molecular weight and this quantity is termed the Number Average Relative Molecular Mass. The conventional notation, M_w rather than the ISO notation, has been employed for this publication.

[2] Certain equipment and instruments or materials are identified in order to adequately specify experimental details. Such identification does not imply recommendation by the National Institute of Standards and Technology nor does it imply the materials are the best available for the purpose.
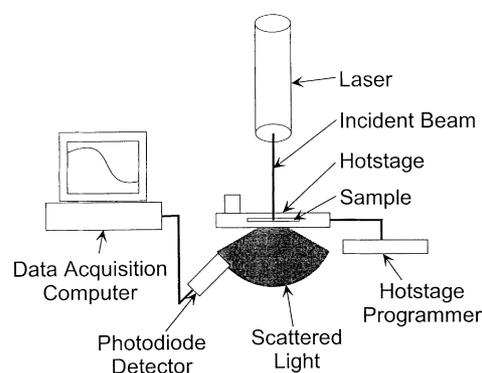
Fig. 1. Schematic of the primary components of the cloud point apparatus.

the size of the uncompounded particles was on the order of 10–50 µm as observed under an optical microscope. Two different surface treatments were applied to the fumed silica via chlorosilane reactions. PS ($M_w = 85,000$ g/mol) terminated with a trichlorosilane end unit, and BMDMCS (Gelest, Inc.)[2] were reacted with the fumed silica in separate reaction vessels. 5% stock solutions by mass of silane in toluene were prepared under dry box conditions for each of the silanes. 0.5 g of untreated silica (predried at 150°C under vacuum for 4 h) was added to 20 ml of the desired stock solution. The resulting suspension was refluxed for 24 h. After 24 h, the suspension was poured into a Teflon dish and the solvent was allowed to evaporate to dryness, after which the treated silicas were stored under vacuum at room temperature.

Compounding of the polymer blends with the fillers was performed in a DACA Microcompounder[2] at 130°C at a screw speed of 100 rpm for 10 min. All relative filler to total polymer concentrations are reported as % mass fractions of filler unless otherwise noted. Cloud points were determined on a small portion of the sample placed on a microscope slide heated on a microprocessor controlled Mettler hot stage.[2] The cloud point apparatus is shown schematically in Fig. 1. The apparatus consists of a single position photodiode detector that monitors scattered light intensity as a function of temperature. The temperature at which the scattered light intensity increases (on cooling) or becomes negligible (on heating) is defined as the "cloud point temperature" (It is noted that either particle clustering or blend phase separation can lead to sample clouding.). The temperature of the hotplate was not monitored, but was high enough for the samples to be in the one phase region. A cover slip was placed over the liquid on the microscope slide and the sample removed from the hotplate. The cover slip was pressed down slightly to squeeze out air bubbles. For each sample, two different heating rates (+0.5°C/min and +0.2°C/min) and two different cooling rates (−0.5°C/min and −0.2°C/min) were utilized to assess any rate dependence in the cloud points. No significant or systematic rate dependence was observed in the cloud point measurements reported here.
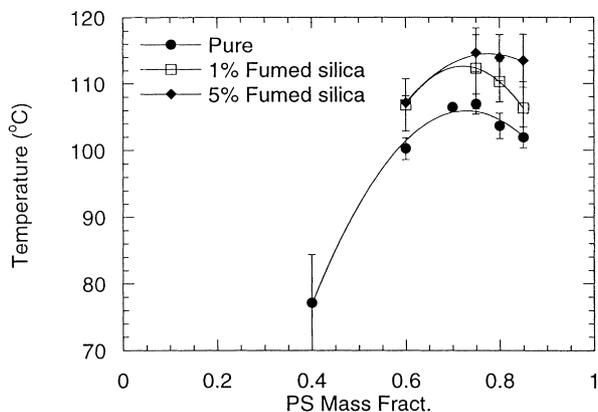
Fig. 2. Cloud point curves for the PS:PB blend—unfilled (●); with 1% untreated, fumed silica (□); with 5% untreated, fumed silica (◆). Solid lines represent smooth fits to the data. Bars on data points indicate ±(one standard deviation.

3. Results and discussion

The cloud point curve for the *unfilled* PS:PB blend is shown in Fig. 2. The critical temperature, T_c, and critical composition, ϕ_c, of the pure blend are estimated to be 106°C and 70% (PS mass fraction), respectively. Also shown in Fig. 2 are the coexistence curves for the same blend with two different concentrations of fumed silica added (mass fractions of 1 and 5%). The addition of the fumed silica shifts the coexistence curve vertically relative to the pure blend, expanding the immiscible region of the phase diagram. We note that if the phase boundary shifts vertically through the addition of filler, then the shift of the critical temperature does not depend appreciably on the relative polymer composition. Our observations on the phase boundary shift in a filled blend then differ from those made by Nesterov et al. [9,10]. The observed critical point shift blend with fumed silica filler is consistent with theoretical estimates of blend phase boundary shifts with small molecule
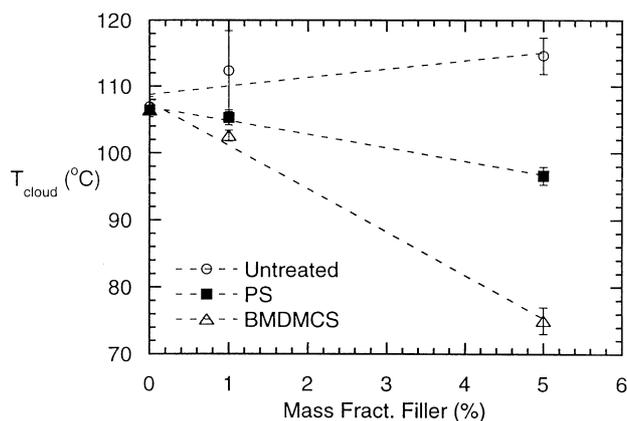
Fig. 3. Comparative shift of cloud point temperatures of a PS/PB blend (70:30 composition) with untreated and treated fumed silica additives. The 0% data represents the unfilled blend. Symbols represent—(○) untreated fumed silica; (■) PS grafted fumed silica; and (△) for BMDMCS treated fumed silica. Dashed lines are linear fits to the cloud point shifts.

additives [6] and with previous measurements on PS/PB blends with a block copolymer additives [12] (The blend measurements normally involve symmetric block copolymers where blend stabilization rather than destabilization is normally observed.). It would be interesting to see whether filled blends resemble blends with block copolymer and other surfactant additives in other ways.

We next make a preliminary examination of the effect of surface-functionalizing the silica particles. The measurements in Fig. 3 show the cloud point temperatures for a fixed blend relative composition blend (70:30 PS:PB) containing 1 and 5% compositions of the surface treated filler particles. While the untreated fumed silica produces an upward shift in the cloud point curve relative to the unfilled blend (Fig. 2), the fumed silica with PS grafted to the surface leads to a slight decrease in the cloud point temperature for the polymer and filler compositions investigated. The BMDMCS treated fumed silica measurements show an even greater decrease in the cloud point for the same polymer and filler compositions. (The whole cloud curve for a range of polymer and filler compositions must be considered as in Fig. 2 to estimate the critical temperature shift with filler additives. This is especially true in the present instance where appreciable polymer segregation to the particle surfaces might be expected to shift the effective critical composition.) Although the measurements on the surface-functionalized particles are incomplete, they show that varying the surface chemistry of the fumed silica filler particles can produce a wide range of variations in the blend phase boundary. Quantitative studies of the influence of surface-functionalization on phase boundary modifications induced by filler requires an improved means of controlling the surface coupling reaction extent, rigorous methods for controlling moisture uptake by the filler and a greater control of filler particle shape and dispersion.

Calculations of the shift of the critical temperature in an Ising-type model with bond and site type "filler" additives having a general interaction (relative exchange interaction) indicate a linear shift of the critical temperature T_c for low volume fractions of additive [5,6]. The slope can be positive, zero or negative, depending on the filler interaction with the fluid mixture [5,6]. This linear concentration dependence of T_c shifts in filled mixtures is also exhibited in phase boundary shifts in blends containing block copolymer additives [6]. An estimated bound on the magnitude of the T_c shift can be inferred from the diluted Ising model which indicates that the magnitude of the slope of the critical temperature shift at low concentration (volume fraction) should be no greater than about three [5]. This estimate is restricted to compact particles that are not too aspherical. The use of this estimate assumes that the molecular weights of the blend components have little influence on the phase boundary since the blend components undergo large fluctuations near the phase boundary. Explicit calculations for block copolymer additives in blends support this approximation [6]. From this argument, we expect the maximum

shift of T_c for 1 and 5% volume fraction filler dispersion to be less than 12 and 60°C, respectively (The density of both polymer and filler have a similar order of magnitude, so that theoretical volume fraction estimates are not too different from experimental mass fraction values.). This bound is in accord with our data where a maximum cloud point T_{cloud}-shift of about 15°C was observed for 5% filler. (We again caution that a cloud point point shift cannot generally be equated to a critical temperature shift.)

4. Conclusions

The upper critical solution phase boundary of a PS:PB polymer blend is destabilized by the addition of untreated fumed silica. Preliminary measurements show that the cloud point temperature of a PS:PB blend with surface-functionalized fumed silica decreases (becomes "stabilized") for the filler and polymer compositions investigated. The alteration of blend phase boundaries through the addition of filler particles has potential ramifications for controlling the properties of filled polymer blends.

Future studies should address questions related to the role of particle shape, dispersion, and size on the phase separation process. This will require model fillers with well-defined surface chemistry, shape, and density of active sites. The shifts of the phase boundary at higher filler concentrations can be large in solvent diluted blends [12,13] and similar changes should be found in filled blends near the particle percolation threshold. This effect has been studied in magnetic phase transitions with filler ("impurities") [14–17]. It is also possible for the character of the critical phenomena associated with phase separation to become significantly modified by the addition of filler [18–22]. The rate of phase separation can be made faster, slower or pinned depending on the particular filler concentration and polymer filler interactions, making the kinetics of phase separation also worthy of investigation.

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