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Material Properties

Controlling final morphologies of two-step polymerization induced phase separated blends of trimethylolpropane triacrylate/acrylate copolymer through copolymer molecular weight

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ABSTRACT

Effect of molecular weight of a thermoplastic copolymer on final morphology of polymerization induced phase separation of trimethylolpropane triacrylate/copolymer blends have been studied. Two acrylate copolymers, ACHM and ACLM, mainly based on methyl methacrylate, butyl acrylate and styrene were synthesized with high and low molecular weight, respectively. Final morphology of TMPTA/ACHM and TMPTA/ACLM blends were investigated by optical microscopic observation of ensemble of surface and bulk phase separation status points of view. Image analysis were done to provide related characteristic length scales.

Polymerization induced phase separation of TMPTA/ACHM and TMPTA/ACLM resulted in different final morphologies with different characteristic length scales, which was attributed to the kinetic effect of the copolymer chains mobility during two-step phase separation induced during the thermal history and UV-irradiation periods.

1. Introduction

The physical, mechanical, electrical, optical and other properties of phase separated multi-component polymer materials strongly depend on their final morphologies [1]. One of the promising ways to obtain such materials is polymerization induced phase separation (PIPS), in which concentration fluctuation grows very fast and phase separation proceeds to some extent until spontaneous pinning gradually freeze the structures. This kind of phase separation belongs to the classification of viscoelastic phase separation, introduced by Tanaka [4–10].

In photo-polymerization induced phase separation (photo-PIPS), cross-linking reactions are controlled by light, which is utilized as a useful tool for controlling characteristic length scale and symmetry of the morphology [2,3]. Here UV-light irradiation and spontaneously photo-polymerization/photo-cross-linking reactions of the system are suppressed as viscosity raises. Consequently, competition between two main antagonistic interactions becomes important: phase separation and vitrification. The former is originated from decrease in mixing entropy of the system which conducted to thermodynamic instability and latter is the result of increase in mixture viscosity as polymerization and cross-linking reactions take place in the mixture [11]. Thus if diffusion can occure properly at the beginning of phase separation, partially or fully immiscible phases would be reached, whose extent depends on the gelation occurrence that freezes morphology by auto-acceleration of chemical reactions [12]. Consequently, it is possible to tune final structure and properties by balancing thermodynamics and kinetics of PIPS [13–23]. This method has been used recently to obtain 2D and 3D bi-continuous gradient morphologies on the surface or in the bulk of polymer blends [3,24–26] but no ordered patterns with more than one characteristic length scale through photo-PIPS have been reported yet.

In this paper more basic investigation of new approach of controlling final morphology through two step phase separation induced by initially mixed thermal- and photo-polymerization and secondly, photo-polymerization under UV-irradiation, were done on the blends of TMPTA and synthesized acrylate copolymers. Two blends were studied, TMPTA/ACHM and TMPTA/ACLM, in which ACHM and ACLM have had similar chemical composition but different molecular weights. The effect of molecular weight of copolymers on final morphologies and their characteristic length scales were studied.

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2. Experimental

2.1. Materials and synthesis procedure

2.1.1. Thermoset network

Trimethylolpropane triacrylate monomer (containing 200–300 ppm MEHQ, Double Bond Chemical, Taiwan) and Irgacure 4265 photo-initiator type I(BASF, Germany), 1 wt% TMPTA, were used. No further purification was done on raw materials.

2.1.2. Thermoplastic acrylate copolymers

Two acrylic copolymers, ACHM and ACLM, with same monomer content but different molecular weights were synthesized through procedure explained in Acrylate copolymer synthesis part of Supporting Information.

2.2. Instrumentation

To characterize the synthesized copolymers, ACHM and ACLM, their films were applied with 60 μm wet film thickness by film applicator (Erichsen, Germany) on dry and clean glass plate substrates, which were conditioned for 72 h in laboratory and 1 h in 333 K oven before film application. After cooling down to ambient temperature, they were immersed for 1 h in water to provide free films which were then dried by absorbent paper followed by spending 2 h at 333 K.

Fourier Transform Infrared Spectroscopy - FTIR (SRG 1100C, Bomem, Canada) was used to characterize the chemical structures. Determination of average molecular weights (Mn and Mw) and polydispersity indices (PDI) were done by Gas Permeation Chromatography-GPC (Waters, USA). Furthermore, glass transition temperatures (Tg) were measured by Differential Scanning Calorimeter-DSC (DSC1-STAR^e system, Metler-Toledo, USA) at a heating rate 10 K/min.

For investigating final morphologies of TMPTA/copolymer blends, they were applied by film applicator with 60 μm wet film thickness on dry, clean glass plate substrates. After spending desired thermal history, they were exposed to UV-irradiation in a homemade UV-cabinet equipped to a medium pressure Hg-lamp with spectrum at 365 nm. The UV-Dosimeter (UV-int150, UV-design, Germany) was used to measure UV-intensity during both thermal history and UV-irradiation; UV-intensity of 2.3E-05 mW/cm^2 and 3.0 mW/cm^2 were obtained, respectively.

Optical Microscope-OPM (DMRX, Leica, Germany) was used to provide images of the films (collectively surface and bulk) in transmission mode by ×400 magnification. Resultant images were analyzed by Image J software (1.47 version) to produce 2D-FFT power spectrum and by its ‘Radial Profile’ plug-in the rotational-averaging process was done to reduce the noise [24]; resulted data were then analyzed by OriginPro software.

2.3. Sample preparation

Mixture of TMPTA and photo-initiator Irgacure 4265 was prepared (called TMPTA). TMPTA/ACHM and TMPTA/ACLM blends were made with 1, 3, 8 and 15 wt% copolymer content. To reach homogeneous mixtures, they were kept in 313 K oven overnight and stirred by magnetic stirrer for 15 min afterward. If needed, blends were stored in opaque white polyethylene containers (O.W.PE. containers) under laboratory ambient condition (293–298 K and 15–25% relative humidity) to spend thermal history. Glass substrates were washed by soap and water, dried and cleaned by acetone. Blends were applied on them and spent 24 h conditioning time followed by 30min in 323 K oven. After cooling down to ambient temperature, they were exposed to UV-irradiation in the UV-cabinet.

3. Result and discussion

3.1. Characterization of copolymers

FTIR spectrums of synthesized ACHM and ACLM samples were obtained and analyzed; presented in FTIR analysis part of Supporting Information. Results show the achievement of similar chemical structure for both. Tg of the copolymers were measured 299 K and 303 K, respectively; presented in DSC analysis part of Supporting Information. Also Mw of 27000 and 12200 were measured for them, respectively; presented in GPC analysis part of Supporting Information.

Tg of ACHM and ACLM are close but ACHM has lower Tg. Note that radical initiators used for production of ACHM and ACLM were different from the viewpoint of half-life times [30] that has affected the ordering of the monomers in their chains which results in different inter-molecular interactions. Existence of hydrogen bonding in ACLM structure is confirmed by FTIR spectrum, that in turn is conducted to its higher Tg [27–29].

In TMPTA/ACHM and TMPTA/ACLM blends, the compatibility of the copolymers with TMPTA-network are equivalent, which means thermodynamically similar instability. Whereas from kinetic point of view the lower the molecular weight, the higher the molecular mobility, that leads to more facile phase separation. Since Mw of ACLM is about half of ACHM, it is expected that under the same condition TMPTA/ACLM blend phase separation goes to the further extent compared to TMPTA/ACHM blend.

3.2. Investigation of TMPTA/copolymer blends final morphologies

At first, TMPTA/ACHM and TMPTA/ACLM samples containing 1, 3, 8 and 15 wt% copolymers were applied on glass substrates just after preparation and exposed to UV-irradiation. Based on OPM images, phase separation has reached much lower extent in these samples compared to samples spending thermal histories before UV-irradiation, which will be discussed below.

By storing samples in O.W.PE containers, initially mixed thermal- and photo-PIPS during thermal history could proceed before secondary photo-PIPS during UV-exposure and morphology freezing. So TMPTA/ACHM and TMPTA/ACLM blends containing 1, 3, 8 and 15 wt% copolymer were prepared, passed thermal histories for 15 or 105 days, then applied and UV-irradiated, Figs. 1 and 2.

As it can be observed in Fig. 1, for both sample series, PIPS has occurred and at the same copolymer content final morphologies are somehow similar but in ACLM containing samples morphologies seems to be more mature and regular.

Longer thermal history offers enough time for developing initial mixed thermal- and photo-PIPS, Fig. 2, in which bi-continuous structures can be observed in most of the both sample series. Note that in the TMPTA/ACLM samples again more mature and regular morphologies have been appeared, which means reaching deeper instable situation in phase diagram.

In Fig. 2, samples containing 1 wt% ACHM or ACLM have droplet morphologies with ≈2.1 μm and ≈2.4 μm diameter, respectively; which corresponds to more grown-up domains in TMPTA/ACLM sample. At3 wt% copolymer content, TMPTA/ACLM samples tends to form bi-continuous structures whereas in TMPTA/ACHM (3 wt%) sample droplet structure still exists and in TMPTA/ACHM (8 wt%) sample an irregular bi-continuous structure can be observed. It has to be noted that in25 wt% ACHM there were no phase separation; since, even in 25 wt% ACLM containing sample phase separation is observed, which is relinquished to discuss here.

In TMPTA/ACHM blends compared to TMPTA/ACLM, because of