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# INTERPOLYMER COVALENT INDUCED MISCIBILITY OF SILICON-CONTAINING COPOLYMER WITH STYRENE-BASED COPOLYMERS

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## ABSTRACT

Copolymer of 3-(trimethoxysilyl)propyl methacrylate (MSMA) with butyl methacrylate (BMA), **1**, and copolymers of styrene (S) with various ratios of acrylic acid (AA), **2**, were prepared via monomer-starved polymerization. Dynamic mechanical analysis (DMA) and atomic force microscope (AFM) were used to investigate the blending behavior of these two polymers. For 50/50 (wt) blending systems, DMA measurements showed a shift of a two-separated glass transition temperature ($T_g$) inward to each other or only a broad $T_g$, depending on the AA content in **2**. The domain sizes of 2-rich phase decreased with an increase of the AA contents in **2**, as observed by AFM. These results indicated that improved miscibility of these two polymers were obtained, due to formation of interpolymer covalent of Si-O-CO links by reaction of methoxysilane groups presented in **1** with carboxylic acid groups in **2**.

*Key Words*: Silicon-containing polymer; Styrene-based copolymers; Miscibility; Interpolymer covalent.

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## INTRODUCTION

Multi-component polymer systems have been widely used in the world because none of the single components can meet the requirement of practical applications more cheaply and effectively [1]. As one of the multi-component polymers, preparation of composites from the two polymers with vastly different physical properties has attracted great attention for many years. In these systems, compatibility of the two polymers is of paramount importance since it has a direct influence on the physical properties and therefore the application of final products [2]. Several strategies, such as adding some compatibilizers in blending systems [3, 4] and forming interpenetrating networks (IPN) between the two polymers [5], have been employed to improve the compatibility of the polymer components. Improved polymer miscibility can also be obtained through incorporation into the single polymer components with functional groups, which lead to strong adhesions such as hydrogen bonding [6-9] or ionic interactions [10-12] among the macromolecular chains.

Silicon-containing polymers have many attractive properties such as flexibility, low surface energy, good electrical and weatherproofing properties, as well as stability toward heat and chemicals [13, 14]. However, due to their low surface energy, silicon-containing polymers are particularly incompatible with other polymers and therefore, stable blending systems can hardly be obtained by the classical methods [15]. Through formation of IPN with other components, it is possible to obtain very fine-scale morphologies and desirable physical properties [16, 17]. Silicon-based organic-inorganic composites, which would be homogeneous at the molecular level, could be obtained via sol-gel reactions [18-20]. These materials combine the characteristics of both inorganic and organic materials, and thus may have a wide variety of potential applications such as optical materials, crystalline display, and coating films [21-23]. In the system containing $SiO_2$ phase and poly(2-hydroxyethyl acrylate), the addition of tetrakis[2-(acryloxy)ethoxy]silane would lead to grafting between two networks and thus promote phase mixing between the organic and inorganic phases [16].

In this study, a silicon-containing acrylate copolymer was blended with styrene-based copolymers. It is well known that acrylate polymers are incompatible with polystyrene [2]. Incorporation of silicon-containing units into the acrylate backbone would further increase the demixing tendency of the two polymers. However, if strong interaction between the two polymer molecules is introduced, it may prohibit demixing of the two polymers effectively. To test this hypothesis, a copolymer of 3-(trimethoxysilyl)propyl methacrylate (MSMA) with butyl methacrylate (BMA), 1, and copolymers of styrene (S) with various ratios of acrylic acid (AA), **2**, were prepared by monomer-starved methods [24] (Scheme 1). The reaction of methoxysilane groups in 1 with carboxylic acid groups in **2** was used to improve the phase mixing between two copolymers and excessive methoxysilane groups, if existing in copolymer **1**, would undergo moisture-hydrolysis and then self-condensation, leading to crosslinking of the copolymers.
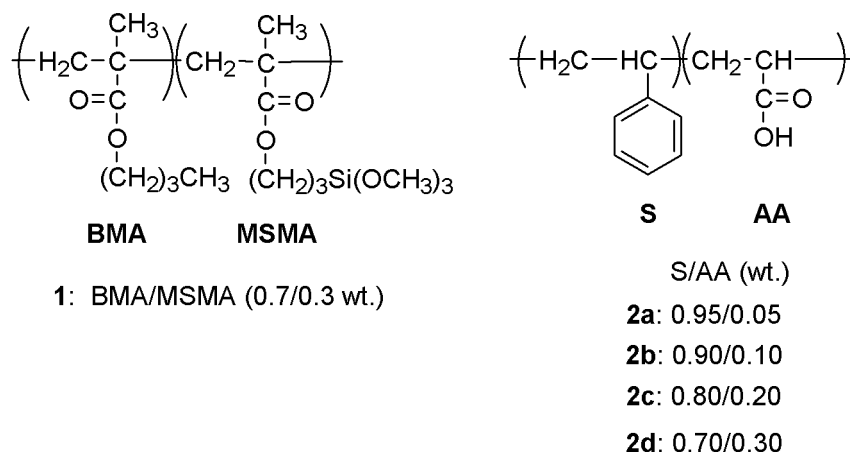
**Scheme 1.**  Structure of copolymer **1** and **2a-2d**.

## EXPERIMENTAL

### Materials

Butyl methacrylate (BMA), acrylic acid (AA), styrene (S) and 3-(trimethoxysilyl)propyl methacrylate (MSMA) were distilled under reduced pressure before use. Benzoyl peroxide (BPO) was purified by recrystallization from choloroform. Azodiisobutyronitrile (AIBN) was recrystallized from ethanol. Benzene was dried over sodium and distilled before use. Tetrahydrofuran (THF) was distilled from Na/benzophone. Dibutyl tin dilaurate (DBTDL) was obtained from Aldrich and used as received.

### Copolymer of 3-(Trimethoxysilyl)Propyl Methacrylate (MSMA) with Butyl Methacrylate (BMA), 1

Copolymer **1** was prepared by a semi-batch, monomer-starved method, similar to the preparation of other acrylic copolymers [24]. 240 ml benzene was added to a flask equipped with a condenser and a blanket of nitrogen. The flask was kept at a constant temperature by the use of an oil bath at 90°C.  A solution containing 140 g BMA and 60 g MSMA in 20 ml benzene was added dropwise in 5 hours, while another solution of 4 g BPO in 100 ml benzene was added over 310 minutes. After an additional 40 ml of  benzene was transferred in, the reaction was kept at that temperature for 2 hours. The resulting polymer was purified by precipitation in *n*-hexane. The final product has the composition of MSMA/BMA similar to the feed ratio, based on elemental analysis. The chemical structure of the copolymers was also characterized by ^{1}H-NMR and FTIR spectroscopy.

## Copolymers of Styrene (S) with Acrylic Acid (AA), 2a-2d

240 ml dioxane was added to a flask equipped with a condenser and a blanket of nitrogen. The flask was heated by an oil bath at 90°C. The solution containing 200 g monomers with various weight ratios of AA to S in 20 ml dioxane was added dropwise over 5 hours, while another solution consisting of 4 g AIBN in 100 ml dioxane was added in 310 minutes. After an additional 40 ml of dioxane was added, the reaction mixture was kept at that temperature for another 2 hours. The resulting copolymer was purified by precipitation from petroleum ether. The contents of AA in copolymers, measured by titration of a copolymer/THF solution with a 0.1 M solution of potassium hydroxide in ethanol in the presence of Thymol-blue as an indicator [6], were similar to the feed ratios for polymerization.

## Film Preparation

All the films have the equivalent weight ratios of copolymer **1** to **2**. Both copolymer **1** and **2** were dissolved in THF, respectively, with a concentration of 0.4 g/ml (for DMA) or 20 mg/ml (for AFM). The solutions were mixed and DBTDL (1 wt% based on the total amount of polymers) was added as a catalyst. After stirring at room temperature for 30 minutes, the solution was cast on a substrate and the solvent evaporated in the air. The film was placed for 7 days in a sealed box with relative humidity of 93%, which was maintained by a saturated potassium nitrate solution [25]. Finally, the films were dried at 60°C for at least 7 days.

## Measurements

Molecular weight was measured using gel permeation chromatography (GPC) with a THF flow and polystyrene standard. Dynamic mechanical analysis (DMA) was performed on a Rheometrices, model RSA II dynamic mechanical tester equipped with low-temperature units using liquid nitrogen as a cooling medium. The films were placed in a sample holder; and 50 to 150 g of pre-tension was added at room temperature to avoid sample buckling. After cooling to –60°C, an additional 70 to 150 g of tension was added, and the measurements were obtained at 5°C increments with ± 0.1% applied strain at 2 Hz. Atomic force microscope (AFM) experiments were carried out using a Nanoscope III scanning probe microscope, Digital Instruments (Santa Barbara, CA, USA). Polymer morphologies were examined by a tapping mode using a DI Multimode under an atmosphere of nitrogen. 15 μl of polymer/THF solution (20 mg/ml) was cast on a silicon wafer by spin coating. To enhance the contrast of AFM image, the dried samples were placed in mixing solvents of $CH_2Cl_2$/hexane (0.8/0.2 vol), with gradual replacement of the solvent by pure hexane until ~ 0.01/0.99 (vol) of $CH_2Cl_2$/hexane.

## RESULTS AND DISCUSSION

Copolymer **1** and **2** were synthesized by free radical polymerization under semi-bath, monomer-starved conditions. A similar method was employed to prepare acrylic copolymers containing fluorinated monomer units [24]. Under this condition, the monomers were added under starved-feed conditions, which could ensure the steady-rate concentration of monomers in the reaction mass and finally, lead to identical compositions for all polymer chains. Furthermore, this preparation method would improve the compatibility of different monomer units, although statistically a few polymer blocks of any appreciable length might still exist in the copolymers. Table 1 lists the molecular weight and polydispersity of the copolymers used in the study.

Copolymer **1** contains 30 wt% MSMA, while copolymers **2a, 2b, 2c,** and **2d** have a AA-unit content of 5, 10, 20, and 30 wt%, respectively. The films prepared by equivalent weight ratios of **1** and **2a-2d** thus have different ratios of MSMA to AA. After two polymers were mixed, the methoxysilane groups of MSMA present in **1** were allowed to react with the carboxylic acid groups of AA in **2**, resulting in grafting and crosslinking structures through formation of Si-O-CO links, which played an important role in improvement of compatibility between the two copolymers. Since this monomer-starved polymerization granted homogeneous distribution of the monomer units of MSMA and AA in macromolecular chains of copolymer **1** and **2**, respectively, it was reasonable to expect that Si-O-CO links between copolymers **1** and 2 had a relatively homogeneous distribution. Excessive methoxysilane groups in **2** would undergo hydrolysis and condensation reactions, leading to further crosslinking structures.

DMA was used on these polymer materials to assess any changes caused by formation Si-O-CO links between polymer **1** and **2** and to get a rough relationship between proportions of Si-OCH$_3$/COOH and miscibility of polymer **1** and **2**. For measuring glass transition temperature (T$_g$) of polymers, DMA shows a greater sensitivity than DSC [26]. Single-component polymer has one T$_g$ in DMA curve, while two-component polymers, if phase separations exist, exhibit two T$_g$, one for each phase of a component. Overall compositions and continuity of two phases affect the modulus drop in glass transition range. Molecular mixing of two poly-

***Table 1.*** Preparation Condition and Characterization of Copolymers **1** and **2**

| Copolymer | Monomer | Feed Ratio (wt) | M$_w$ [a] | M$_w$/M$_n$ [a] |
|---|---|---|---|---|
| 1 | MSMA/BMA | 0.3/0.7 | 8,200 | 1.65 |
| 2a | S/AA | 0.05/0.95 | 7,400 | 1.57 |
| 2b | S/AA | 0.1/0.9 | 6,900 | 1.83 |
| 2c | S/AA | 0.2/0.8 | 7,300 | 1.60 |
| 2d | S/AA | 0.3/0.7 | 7,800 | 1.68 |

[a]Measured using GPC with THF flow and polystyrene standard.

mers will lead to shift or broadening of the transitions. Therefore, incompatible materials show two relatively sharp transitions at the same positions as of single polymers, while the partial miscible blends may show one broad transition. Since both homopolymers of PS and PAA have a similar $T_g$ near 100°C [27], different compositions of S and AA in the series of copolymer **2** would not cause too much difference in $T_g$ for copolymers **2a-2d**.

DMA curves, showing storage modulus (E′) as a function of temperature for these materials, are presented in Figure 1. The series of two-component polymers, based on various ratios of Si-OCH$_3$/COOH, are supposed to have different density of Si-O-CO links between two polymers. For copolymer **2a** containing 5 wt% AA, the material, prepared by equivalent weight ratio of **1/2a**, exhibited two fall-down ranges in E′ curve of DMA. This indicated existence of 2 $T_g$ in this system due to the phase separation of the two polymers. The one near 25°C belonged to copolymer **1** and the other near 100°C could be ascribed to **2a**. With the weight ratio of AA in **2** increasing to 10 wt%, the 2 $T_g$'s shifted inward to each other and the transition ranges became somewhat broader (**1/2b** of Figure 1). This could be explained as an increased mixing of two components due to the formation of more Si-O-CO links between the two polymers. A further increase of AA to 20 wt%, as shown in **1/2c** of Figure 1, the $T_g$ at higher temperature continued shifting to the middle but the $T_g$ at lower temperature did not shift further.

In the case of copolymer **2d** containing 30 wt% AA, only one very broad glass transition range, where E' gradually fell down, could be found for **1/2d** materials. This might suggest the degree of mixing for these two polymers on micro-phase scale or molecular scale, although the glass transition was not a theoretically single, sharp peak.
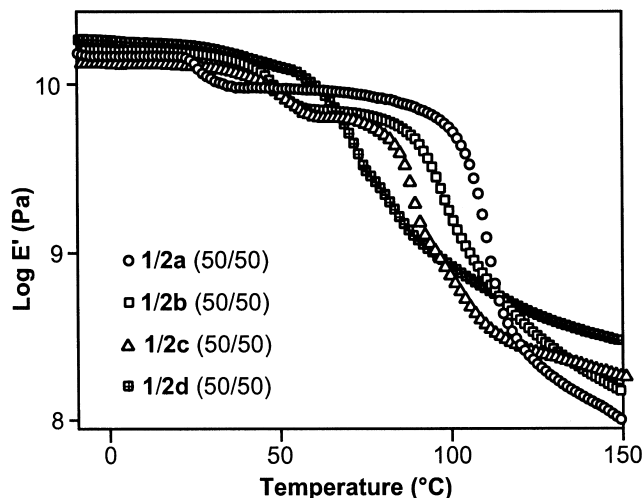


***Figure 1.***    DMA curves of the blending materials of copolymer **1** with **2a-2d**.

It is also worth mentioning that Curve **1/2a** of Figure 1 had the highest intermediate E' value. The explanation might be that copolymer **2a**, which had higher modulus than **1**, formed a continuous phase in this system, and thus made a contribution to the mechanical behavior of resulting materials. An increase of mixing with copolymer **1** of low modulus might reduce the contribution of copolymer **2** series to the modulus of the final products.

To learn the phase behavior further, AFM was used to investigate the morphologies of these materials. The samples prepared by spin coating showed a very smooth surface (Figure 2a). To enhance contrast of the phases, the samples were treated by $CH_2Cl_2$/hexane mixing solvents, with a gradual increase in the proportion of hexane. A similar method was employed in AFM studies on the diblock polymer brush of PS-b-PMMA upon treatment with $CH_2Cl_2$/cyclohexane [28]. In that case, $CH_2Cl_2$ was a good solvent for both PS and PMMA, while cyclohexane was a better solvent for PS than for PMMA. With an increasing cyclohexane content, the PMMA-blocks collapsed and the PS blocks swelled, leading to an increase of surface roughness. It was also claimed that the change of contact angle and surface chemical composition measured by XPS confirmed the reorganization of diblock chains [28, 29]. In our case, copolymer **1** had several covalent connections; the one that might stabilize the thin films under solvent treatment was the tether to the substrate by possible reaction of Si-O-Me with silicon wafer, the other was the Si-O-CO links with copolymer **2**. In addition, these materials might have some semi-IPN structures caused by hydrolysis and self-condensation of MSMA units in copolymer **1**. Here, no intention was made to investigate the effect of substrate on morphologies of the final materials. It was also assumed that the sample treatment by mixing solvent did not lead to lateral movement of phases. Although the content of AA in copolymer **2** had some influence on this treatment of mixing solvent, a much better contrast of phases in AFM images had been obtained in all cases, compared to the untreated samples. This method also facilitated in assigning the phase to each component. Figure 2b shows the AFM image of the sample after treatment by the mixing solvents. Apparently, the sample had a much larger contrast in height AFM image, in comparison with Figure 2a. Different regions could be easily identified; the darker patches were the depressed parts, while the brighter areas are the elevated ones. Based on the assumption that copolymers **1** collapsed and **2** swelled in the treatment with mixing solvents, the darker patches could be assigned to copolymer **1**-rich phases while the brighter areas mainly consisted of **2**.

Figure 3 shows 2-D AFM height images of the samples after treating with mixing solvents to enhance the contrast. With 5 wt% AA in copolymer **2**, the materials showed a large difference in height image of AFM (Figure 3a). Bi-continuous phases of the two polymers could be found in this image, with some small domains of copolymer 1-rich phase dispersed in larger phase of copolymer **2** (darker dots in brighter areas). If the AA content in copolymer **2** increased to 10 wt%, the AFM image (Figure 3b) showed a continuous phase of copolymer **2** (brighter areas) with dispersed phases of copolymer **1** (darker dots). For copoly-
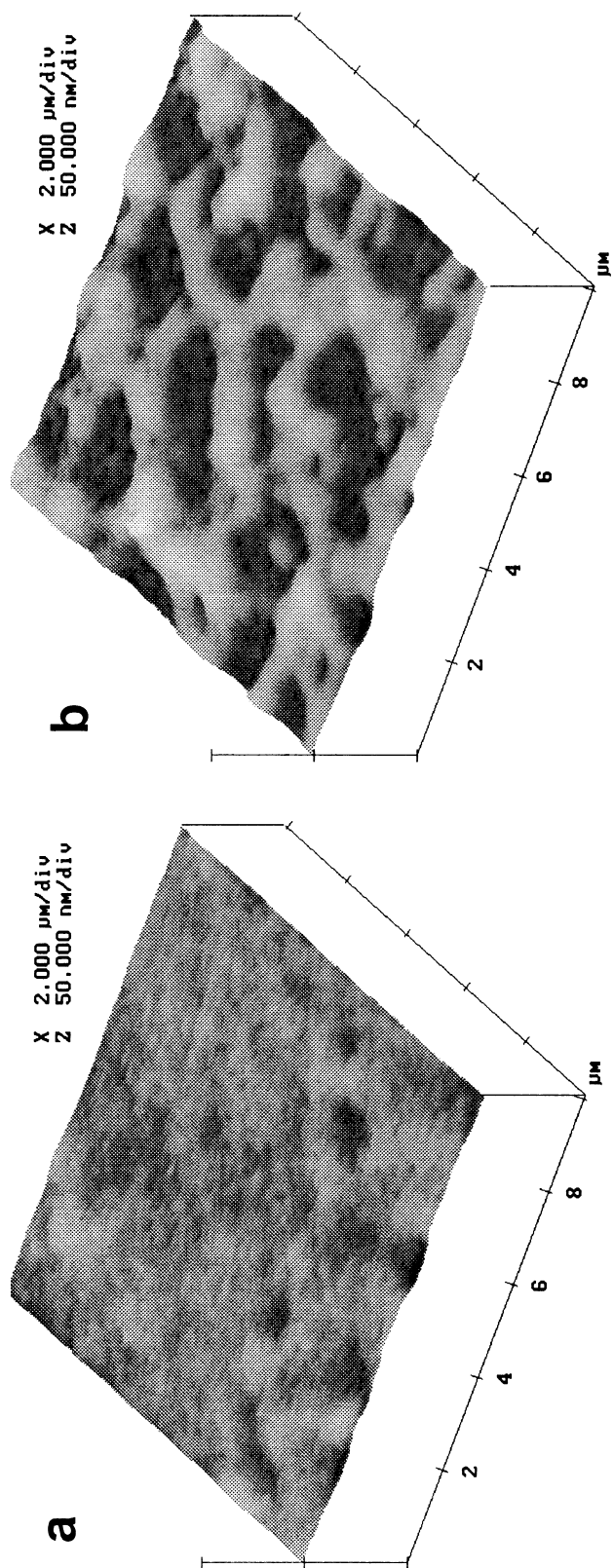
*Figure 2.* Three-dimension AFM images of **1/2a** blending materials (a) as spin casting and (b) after treatment of $CH_2Cl_2/$ hexane with gradual increase of the hexane content.
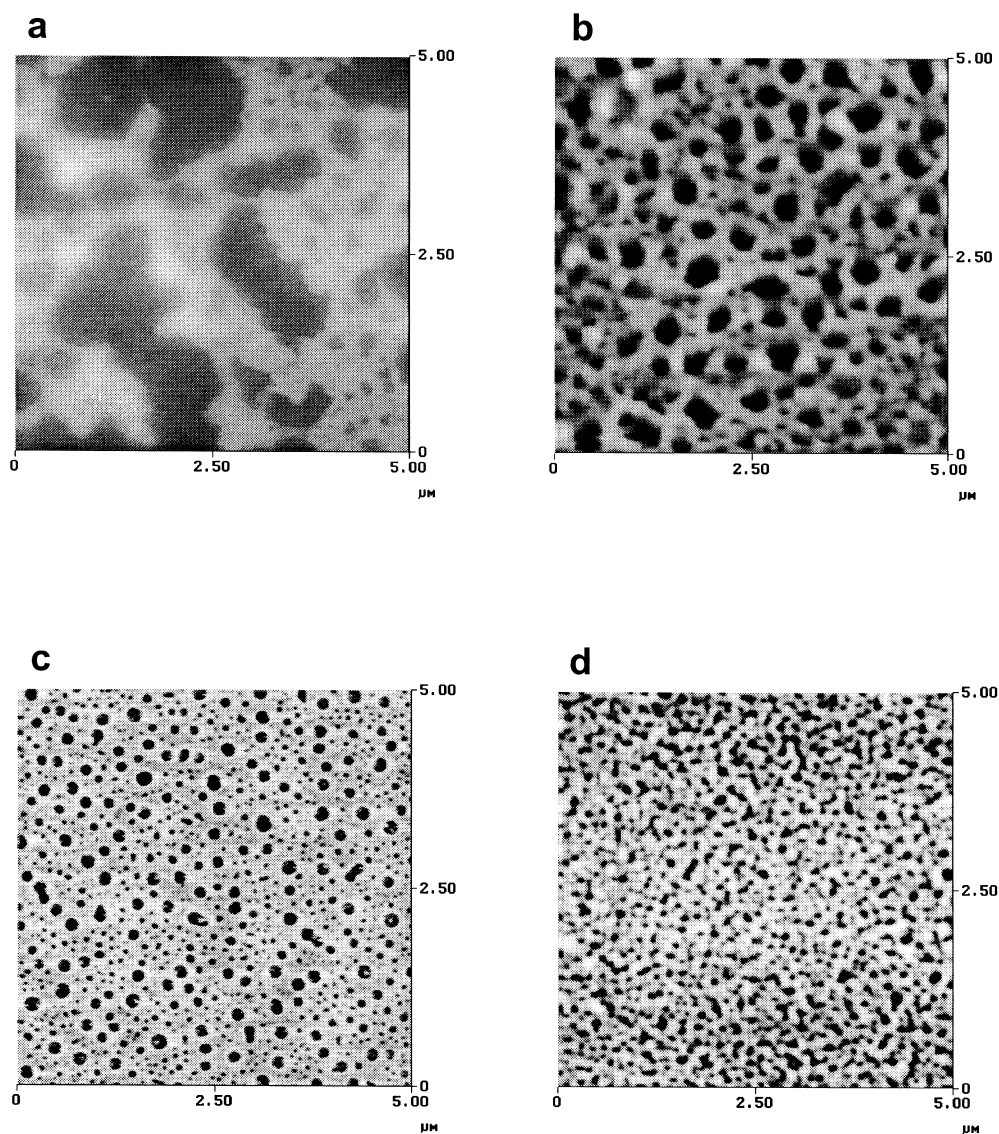
**Figure 3.** Two-dimension AFM images after treatment by mixing solvents of $CH_2Cl_2$ / hexane for the blending materials of (a) **1/2a**, (b) **1/2b**, (c) **1/2c**, and (d) **1/2d** (Z scale: 20 nm).

mer **2c** containing 20 wt% AA, the materials showed circular domains of copolymer **2**-rich phase in the AFM image (Figure 3c). The diameters of the domains, which were smaller than those in Figure 3b, ranged from 50 to 240 nm. A further increase of AA content in copolymer **2** to 30 wt% led to a very fine distribution of phases in the AFM image (Figure 3d), which indicated an increasing degree of mixing of the two copolymers. AFM measurements confirmed the DMA results that an increase of AA content in copolymer **2**, which would lead to an increase of

grafting density between copolymer **1** and **2**, which resulted in improved compatibility of the two copolymers.

## CONCLUSION

Here, a silicon-containing acrylate copolymer was blended with styrene-based copolymers. Interpolymer covalent links of Si-O-CO were introduced between these two polymers by the reaction of methoxysilane groups with carboxylic acid groups. DMA results showed a shift or broadening of glass transition temperature when the ratios of methoxysilane groups to carboxylic acid groups in the materials varied. The morphologies investigated by AFM indicated increase of phase mixing of the two polymers due to the formation of Si-O-CO links. In conclusion, the strong interaction of interpolymer covalent links between these two polymers would lead to increased miscibility of the polymers.

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