Phase Identification and Elastic Property of Blend Copolymer Characterized by Force Modulation Microscopy and Force-Distance Curve

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ABSTRACT

The technique of polymer blending has been used to create new types of polymers with desirable properties in the past decade. Force Modulation Microscopy (FMM) provides a local contrast due to the local elasticity difference of a sample surface in addition to topography information [1]. The mechanical properties are examined continuously over the extended area and force modulation mode is utilized to identify two phases to measure local elastic properties [2]. Poly(styrene-isobutylene-styrene) (SIBS) blended with poly(styrene-maleic anhydride) (SMA) was characterized by Atomic Force Microscopy (AFM) to understand phase identification. Young's moduli of bulk materials were obtained by tensile testing machine from the slope of stress-strain curve [3]. The localized elastic modulus of each phase is obtained by F-D curve through adopting the mathematical theory [4] and image analysis was employed to measure the volume fraction from FMM images at different blending ratios.

Keywords: Force Modulation Microscopy (FMM), Elastic Modulus, Phase Identification, Polymer blends

1. INTRODUCTION

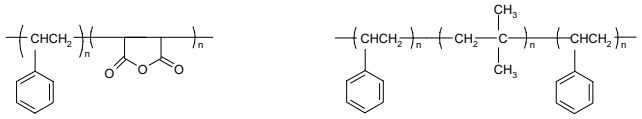
Polymer blending has been a technique used to create new types of polymers with desirable properties. But most polymers are not miscible and as a result will phase separate into their own structural domain. Unfortunately most polymer pairs exhibit poor adhesion between these domains and will ultimately lead to inferior mechanical behavior of the mixture. Therefore understanding the factors that affect morphology and mechanical properties will assist in developing superior plastic materials.

Force Modulation Microscopy (FMM) is an extension of AFM imaging that includes powerful technique for scientific research of the sample's mechanical properties. The FMM image is from the amplitude of the vertical vibration of the tip. It has great resolution for sample features that are difficult in the contact mode of AFM and Electron Microscopy. It is a continuous 2-D mapping of local mechanical properties on nanometer scale. The probe is modulated into contact with a sample and the sample's surface resists the oscillation and cantilever bends.

With Force vs. Distance curves, AFM can distinguish surface regions of different stiffness and adhesion characteristics. In this technique, force applied on the surface is measured by the deflection of the cantilever while approaching and retracting from the surface [7].

2. EXPERIMENTAL

2.1 Sample preparation



SMA **SIBS**

The SIBS1027 contained 26 wt% styrene and SMA, random copolymer, contained 14 wt% maleic anhydride and 86wt% styrene. Polymer blends were made with various compositions as described in Table 1. Each composition was blended from a solution consisting of 10% solids with 65% tetrahydrofuran (THF) and 25% toluene. Toluene was added to prevent moisture or water buildup that may cause the SIBS to precipitate during the mixing stage. The solution was stirring for at least 24 hours. Immediately after the solution was stopped, methanol was used to precipitate the blended polymers. The precipitated material dried for at least 2 days at room temperature and final solvent removal occurred in a vacuum oven at 70°C for at least another 2 days.

In order to perform further testing, the blended material was then compression molded into thin flat sheets. Teflon coated aluminum sheets were used to sandwich the material to produce a flat, smooth surface and prevent the material from sticking to the heated plates. An aluminum mold was used to make a uniform film thickness of approximately 1.3mm. The material was heated at a temperature of 160°C for 25 minutes. Afterwards, approximately 6-7 metric tons of force (1300-1600psi) was applied onto the sample for another 25 minutes. In order to complete the process the material was set aside to cool at room temperature.

Table 1: Compositions of Blends (weight %)

Sample #	SIBS1027	SMA
1	100	0
2	80	20
3	60	40
4	40	60
5	20	80
6	0	100

2.2 Force Modulation Microscopy

This study examined the morphology of SIBS and SMA blends at different compositions by FMM as the two polymers have different elastic properties and these images were compared with Scanning Electron Microscopy (SEM) images. To distinguish the two phases by FMM, samples were embedded in epoxy and polished to produce a smooth flat surface. FMM images were obtained by using on XE-100 microscope manufactured by PSIA Corp. A non-contact tip, stiffer than contact tip, with on silicon cantilever was used. The cantilever's length and width were 125μm and 35μm, respectively. The cantilever had a resonant frequency of 325 kHz and a force constant of 40N/m. Choice of the cantilever is a very critical factor in FMM. Phase and Force Modulation images were obtained at optimized scanning conditions. Image analysis has been carried to measure volume fraction from FMM images at different blending ratios.

2.3 Image Analysis

Image analysis has been carried to measure volume fraction from FMM images at different blending ratios.
The volume fraction of SMA phase was obtained by dividing the area of that phase by the total area of image.

$$\text{Volume fraction of SMA phase} = \frac{\text{Total area of one phase}}{\text{Total area of image}} \times 100 \quad (1)$$

2.4 Elastic Modulus from F-D Curve

Based on the FMM and modulus calculation by the F-D curves, the phase identification can be efficiently verified between the experimental results and the presented values by the F-D data. The slope of curve is a representative of the stiffness of the material. The hard segment, high elastic modulus, has steeper slope than the soft segment.

The cantilever chosen for F-D analysis had a resonant frequency of 105kHz and a force constant of 0.9N/m. The data were acquired at 1.0μm/s down speed and up speed. The regions decided by each phase were measured at the one point and plotted by z-distance and vertical force in the automated computer interface. After analyzing force and distance data, we can obtain the slope of the approaching line which indicates a compression modulus.

3. RESULTS AND DISCUSSION

To characterize the surface morphology of the blend copolymer at the different mixing ratios, SEM and FMM were used. Figure 1 shows that particles ranged from 1-3μm were introduced at the 80wt% SMA in Figure 1(C). But at a concentration of 40wt% SMA in Figure 1(B), the agglomerated particles were no longer present and a co-continuous phase of materials had formed with no defining features. From Figure 1, two phases were difficult to detect with SEM.

However, the FMM results provided further evidence of phase separation between the SIBS/SMA force modulation microscopic images. FMM images revealed differences between the two phases clearly, even though SEM did not show any phase separation images due to poor contrast of two phases.

From the image analysis by GAIA Blue software with FMM image, the volume fraction of SMA was calculated as 18.8% for Figure 1(a), 42.5% for Figure 1(b), and 77.0% Figure 1(c). These values are in good agreement with blending ratio used to formulate the blends.

The microstructure depended on the composition of the blend, compatibility of the two components, fabrication of the blended materials, and the physical properties of the two polymers. Figure 2 shows the Young's Modulus of bulk materials at the different mixing ratio. Small amounts of SMA do not greatly affect the modulus. From 26.7wt% SMA, the modulus increased dramatically.

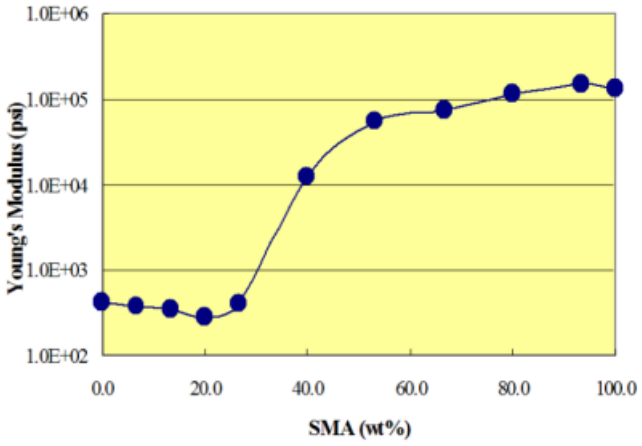


Figure 2: Effect of SMA compositions on Young's modulus from composite materials.

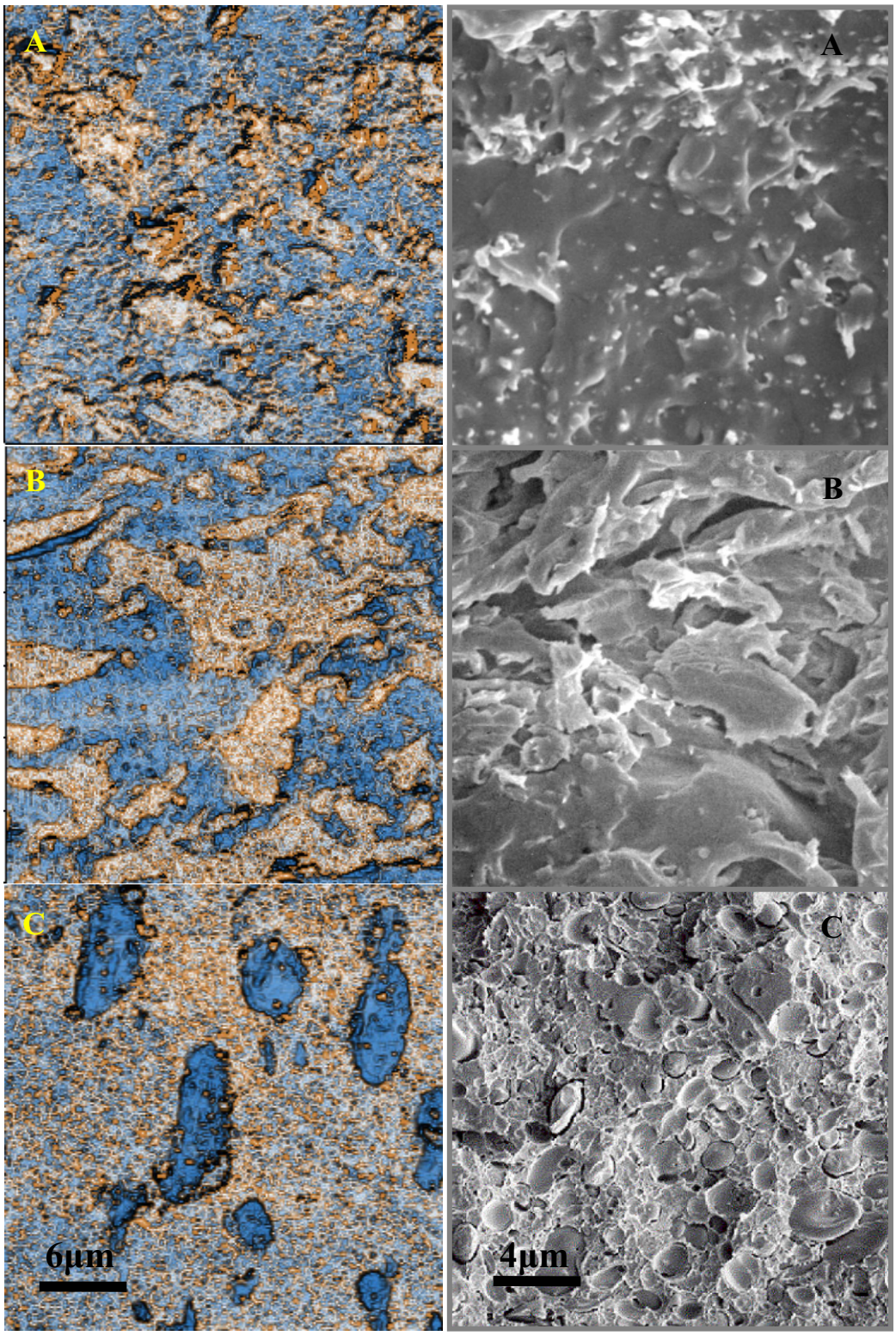


Figure 1: FMM images for phase identification of (a) 20wt% SMA/80wt% SIBS1027, (b) 40wt% SMA/60wt% SIBS1027, and (c) 80wt% SMA/20wt% SIBS1027.

The evaluation of mechanical properties with the AFM has been purely qualitative. The operation of the AFM in force modulation mode allows for a more quantitative characterization of polymer behavior under mechanical loads. This quantitative information gives more confident for phase identification.

The verification of phase identification in the FMM images is important for polymer blends. Even though FMM images show the information of phase separation, we cannot identify each region clearly. In terms of F-D analysis, the comparison of stiffness is able to identify those phases of polymer blends.

In Figure 3, the F-D curve represents the vertical trail of AFM tip's movement. According to this analysis, the data for approaching the tip were collected to analyze the comparison with 1024 data points. The local elastic modulus of the sample is determined from the slope of the initial portion of the force-distance curve as the AFM tip comes into contact with the sample surface.

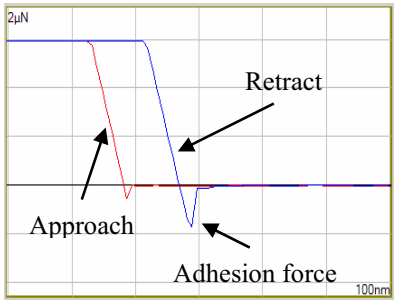


Figure 3: Typical force versus distance curve of SMA / SIBS blends

By means of the linear fitting from the portion of approaching line, the moduli were obtained for each phase. Figure 4(a) shows that the slope of F-D curve, which means the modulus, is 1.785 N/m for the 80 wt% of SMA. The modulus of 20 wt% SIBS is 1.040 N/m. The difference of each modulus is 0.75 N/m. In other words, the SMA phase is 1.7 times bigger than SIBS phase. Consequently in the FMM images, the brighter contrast shows SMA phase, hard segment, and the darker contrast reveals SIBS phase, soft segment. Therefore, we can clearly identify each region of SMA and SIBS qualitatively. FMM images could be easily analyzed due to the stiffness of SMA and SIBS.

4. CONCLUSIONS

The microstructure depended on the composition of the blend, compatibility of the two components, fabrication of the blended materials, and the tensile properties of the two polymers. FMM images clearly revealed differences between the two phases because of various elastic moduli, while secondary electron images of SEM was not clear to show phase differences due to poor contrast. FMM is proved to be a unique and powerful method to characterize phase separation of polymer blends. From F-D curve of each phase, the local mechanical properties such as modulus were compared between the two phases. Therefore, the phase identification in the FMM images can be proved by combining the force analysis of AFM.

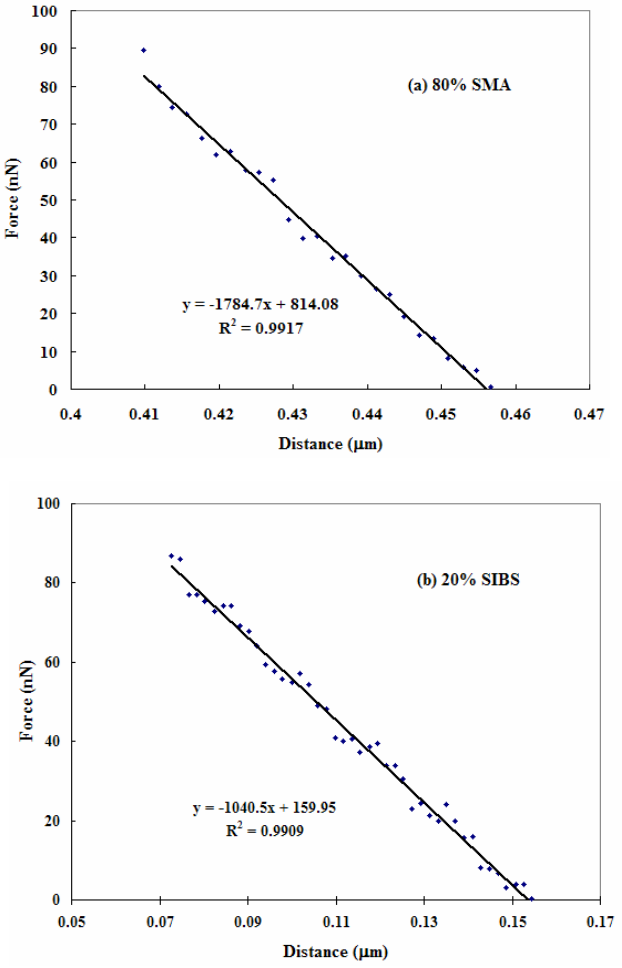


Figure 4: Linear fitting of tip approaching region, blend ratio of SMA/SIBS = 80/20

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