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The application of micro-thermal analysis technique in the characterization of polymer blend

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Abstract

Micro-thermal analysis (TA) is an exciting new innovation in the field of materials characterization. It combines the visualization power of atomic force microscopy (AFM) with the characterization capabilities of TA. Micro-TA can be used to characterize materials and surfaces, and to visualize the spatial distribution of phases, components, and contaminants in samples such as polymer blends. When two or more polymers are combined (incompatible blend), the microstructure and morphology have a direct impact on the materials final mechanical and chemical properties. Knowledge of the size and distribution of these phases can lead to a better understanding, and ultimately optimization of mechanical properties.

In this study, micro-TA is used to examine the uniformity of high-density polyethylene and polystyrene blend with composition 70/30 and 50/50 (by weight) using different blend methods, including physical blending, blending in an extruder, and blending on a Haake mixer. Since the compatibilizer are commonly used in the polymer industry, the effect of compatibilization of block copolymers on the uniformity of a 70/30 (by weight) blend of high-density polyethylene (HDPE) and polystyrene (PS) is also investigated by micro-TA technique and the results are compared with that from other techniques, including scanning electron microscopy (SEM) and Raman spectroscopy. The compatibilizers investigated are several block copolymers, including poly(styrene-b-ethylene), S-b-E; poly(styrene-b-ethylene/propene), S-b-EP; and poly(styrene-b-ethylene/butene-b-styrene). The results from micro-TA shows the similar trend that from SEM and Raman. The results shows that S-b-E block copolymer is the most effective compatibilizer among the compatibilizer tested, which decreases the domain size of the dispersed polystyrene phase while improving its dispersion in the polyethylene matrix. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Micro-TA; Polymer characterization

1. Introduction

On the macroscopic scale, many multicomponent materials can be thought of as homogeneous. However, when investigated on the microscopic level, these same materials often show distinct chemical heterogeneity. It is very important to know how chemical heterogeneity is shown in the solid-state materials because the chemical composition and architecture decide the characteristics of material. Understanding the distribution relationship of heterogeneous systems is the fundament in the fabrication of advanced composite materials.

Blend polymer are used often in industry to enhance the mechanical properties. To increase the strength of a blend polymer, a homogeneous mixture must be

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obtained. There are three ways in which to mix polymers: (1) physical blend involving large particles, (2) physical blend involving fine particles using a mold and (3) mixing polymers using a chemical known as a compatibilizer. Each end of a compatibilizer has a polymer, which allows it to connect to the original polymer. Therefore, in the last few decades, modification of a polymer blend by compatibilization with inter-facially active compatibilizers (usually block copolymer) has been widely applied in practice [1]. The microstructure and morphology have a direct impact on the materials final mechanical and chemical properties. The information of the size and distribution of these phases can lead to a better understanding, and ultimately optimization of mechanical properties. The stronger the final polymer is, the more homogeneous the blend is.

Many techniques can be employed to evaluate the effect of the compatibilizer on the compatibilization process. Scanning electron microscopy (SEM) is often used in studying uniformity of polymers [2]. However, the sample used in SEM study has to be well prepared, coated with gold to prevent from charging and also the operation of SEM is under vacuum. Raman spectroscopy, on the other hand, had also made the small but the significant contribution in the study of polymer over last 20 years. This technology cannot only provide the detailed information on the structure of polymer, degree of crystallinity morphological changes, copolymer and isomeric composition [3], but also used in the characterization of polymer fibers, analysis of polymer surface, and identification of various layers in a multilayer of laminated polymer [4].

Micro-TA is an exciting new innovation in the field of materials characterization. This invention combines the visualization power of atomic force microscopy (AFM) with the characterization capabilities of thermal analysis [5–8]. In micro-TA, the AFM head is

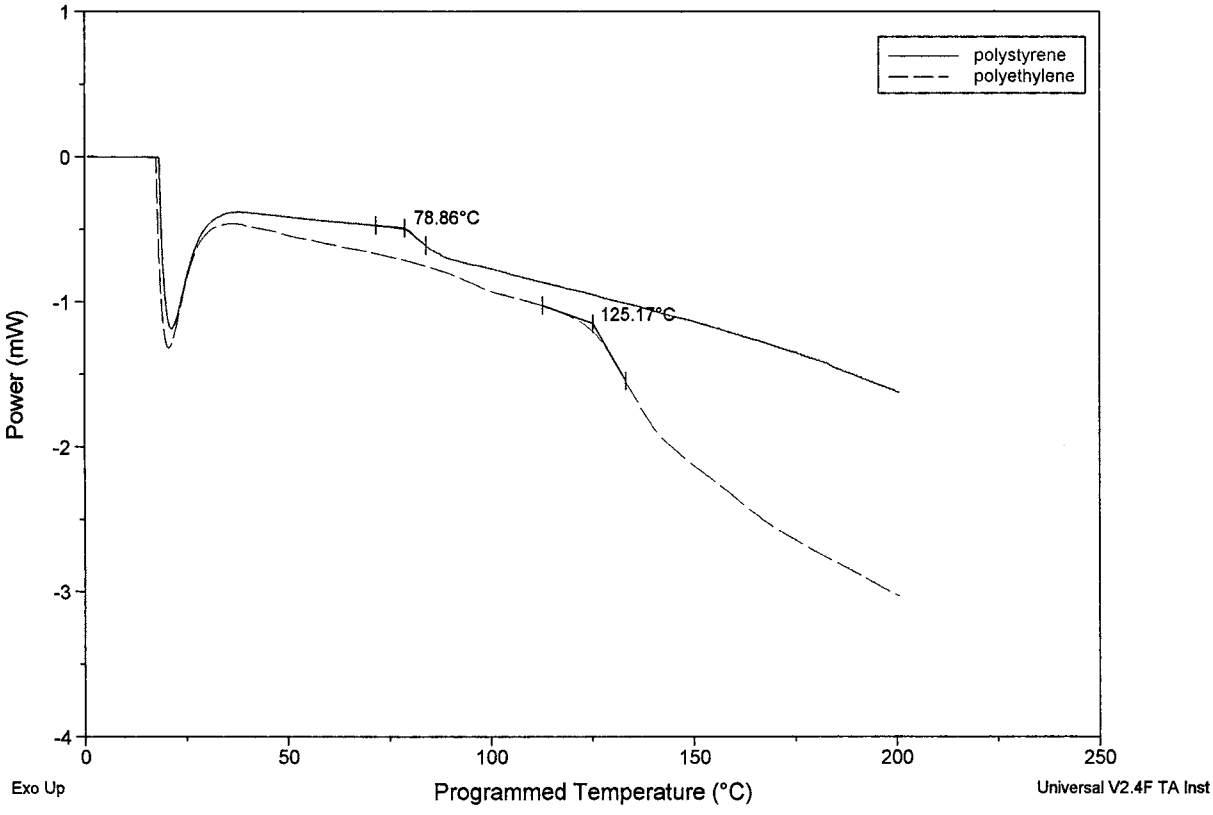

Fig. 1. Micro-MDTA results of HDPE/PS blend.

fitted with an ultra-miniature probe which not only provides the heat source, but also measures the thermal response providing information similar to traditional thermal analysis, but on a microscopic scale.

In this paper, micro-TA is used to study the uniformity of high-density polyethylene and polystyrene blend with composition 70/30 and 50/50 (by weight) using different blend methods, including physical blend, blending in an extruder, and blending on a Haake mixer; and the effect of compatibilization of block copolymers on a 70/30 (by weight) blend of high-density polyethylene (HDPE) and polystyrene (PS). The compatibilizers investigated are several block copolymers, including poly(styrene-b-ethylene), S-b-E; poly(styrene-b-ethylene/propene), S-b-EP; and poly(styrene-b-ethylene/butene-b-styrene). The phases information of blend polymers, such as domain size and distribution, are visualized based on their thermal properties (thermal conductivity) and identified by measuring the materials thermal properties, including glass transition temperature and melting temperature. The results from LRS-1 Raman spectroscopy, JEOL JSM-5400 SEM and micro-TA are compared with each other.

2. Experimental

Micro-thermal analyzer μTA2990 is used to visualize and identify the phases presented in the blend

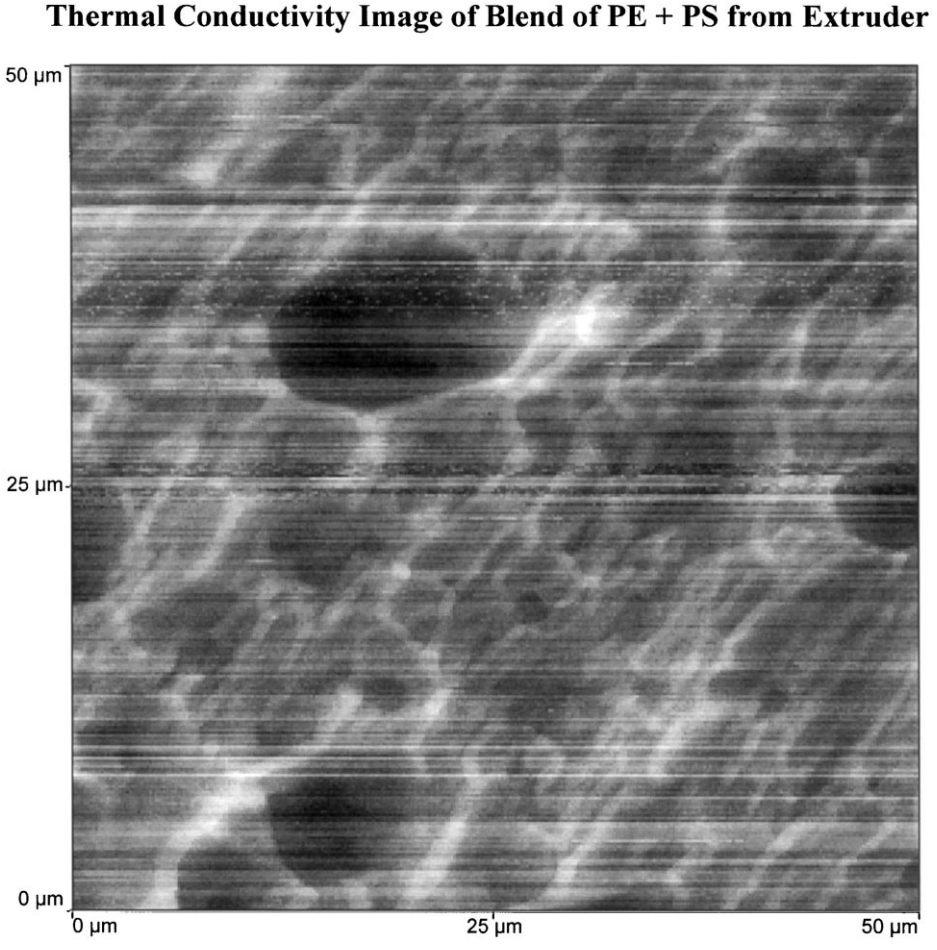

Fig. 2. Thermal conductivity image of HDPE/PS blend prepared from extruder.

polymers. All the homopolymer, including PS, and HDPE, used in this study are the commercial products. PS is styrene 666D from Dow Chemical company with a molecular weights of $M_w = 260\,000$ and $M_n = 60\,000$. HDPE is Eastman Tenite H6001 from Eastman Organic Chemicals. S-b-E is made by MMI S:E = 50:50, poly(styrene-b-ethylene/butene-b-styrene) (S-EB-S) is Shell Kraton G1701X, and S-b-EP is Shell Kraton G1050. The blends (70/30 (by weight)) blend of HDPE and PS are prepared on a 60 ml Haake mixer at 200°C with 100 rpm for 10 min. After blend, the samples are compression molded with a hydraulic press at 200°C at 5000 psi for 10 min.

3. Results and discussion

3.1. The uniformity of polymer blend prepared from different methods

When the components are physical blended in various proportions (20% PS, 80% HDPE; 50% PS, 50% HDPE and 80% PS, 20% HDPE), the individual components can be clearly seen in the blend polymer. Then the melting temperature and glass transition temperature are measured by μTA as shown in Fig. 1, it again confirms that the simple physical blend cannot mix PS and LDPE uniformly.

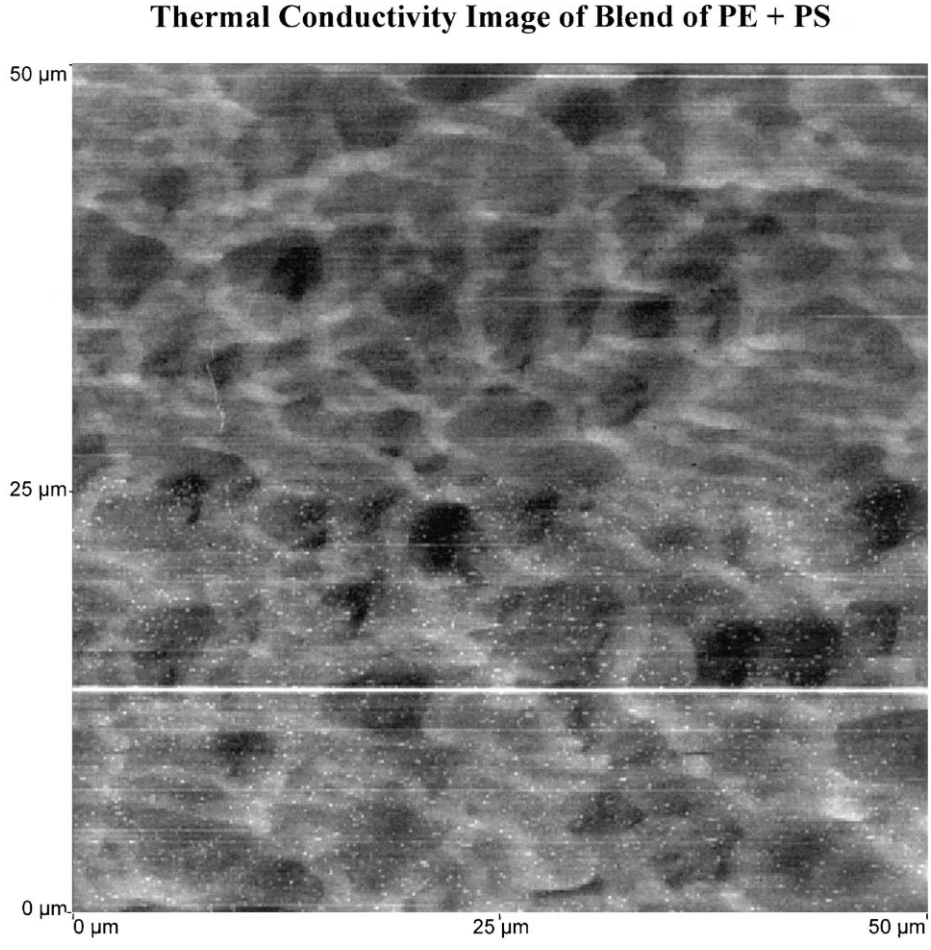

Fig. 3. Thermal conductivity image of HDPE/PS blend prepared from rheometer.

Fig. 2 presents the thermal conductivity images for the HDPE/PS blend polymers prepared in an extruder. The thermal conductivity image shows that PS is dispersed inside HDPE matrix with a broad size distribution and a smooth surface. The average diameter of PS particles is about 7.9 μm.

Fig. 3 shows the thermal conductivity images for the HDPE/PS blend polymers prepared on a Haake–Rhecord 90 torque Rheometer by adding the dry-mixed blend components to a 60 ml batch mixer equipped with a pair of roller. Compared with the previous results, it can be seen that the average diameter of PS particles decreases from 7.9 to 6.4 μm.

In order to have further improvement in the uniformity of blend polymer, 2% S-b-E block polymer is added. It is then found that not only the particle size is greatly reduced, but also the size distribution becomes more uniform for the blends containing the block copolymers, as shown in Fig. 4. The average diameter of PS particles in the HDPE matrix is about 1.3 μm, which is far lower than that prepared from the other methods.

3.2. The effect of compatibilization of block copolymer on the uniformity of polymer blends

Significant decrease in the particle size is shown for all the blend which contain block copolymers, especially for one containing the S-b-E block copolymer as

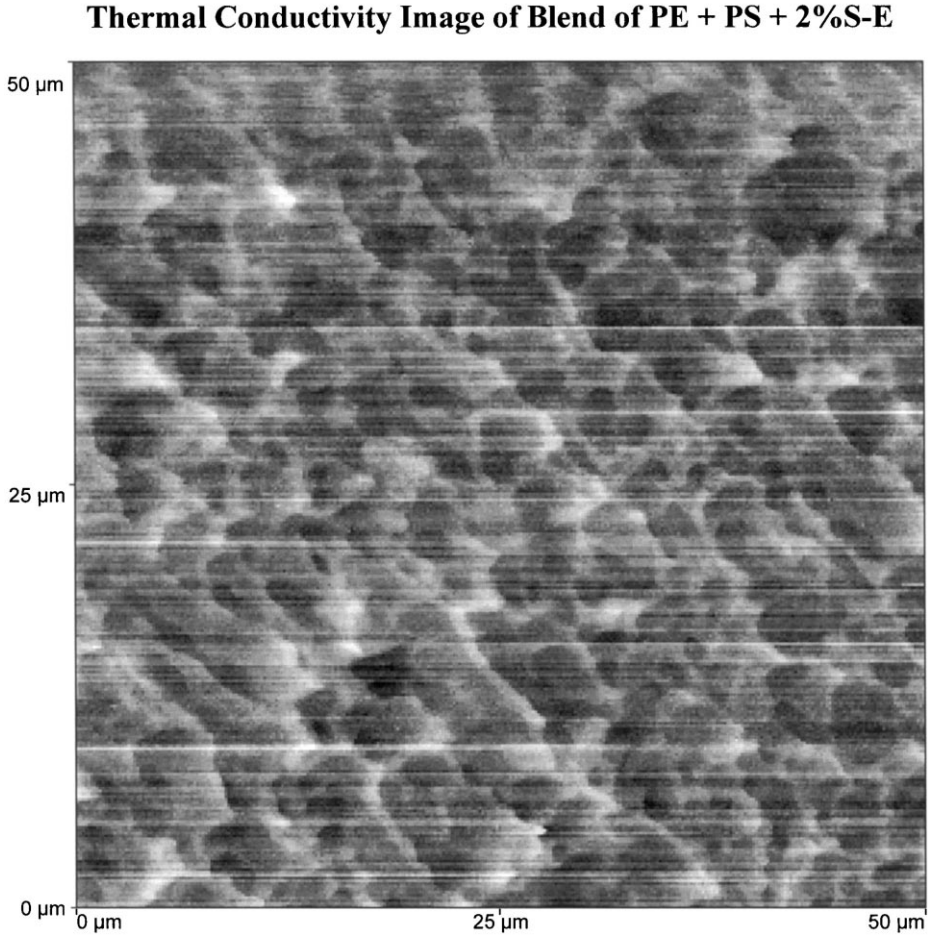

Fig. 4. Thermal conductivity image of HDPE/PS blend prepared with S-b-E block polymer.

shown in Fig. 4, when compared with sample containing no compatibilizer (Fig. 3). The volume-average diameter (d_v) decreased from 6.4 μm of the uncompatibilized sample to 4.1 μm of the sample with S-EB-S, 2.8 μm of the sample with S-b-EP and to 1.3 μm of the sample containing S-b-E. An effective compatibilizer can modify the phase morphology and the interfacial adhesion of a blend by: (1) reducing the interfacial tension between the two phases and hence leading to finer dispersion of one phase in another, (2) enhancing adhesion by coupling the phases together, (3) stabilizing the dispersed phase against coalescence [9,10].

SEM and Raman spectroscopy also can be used to evaluate the effectiveness of a compatibilizer and the compatibilization process [1]. Figs. 5 and 6 illustrates the morphology of the sample HDPE/PS (70/30) no compatibilizer and the sample HDPE/PS (70/30) with 2% of S-EB-S block copolymers. The result from SEM is agreeable to that from micro-TA, which indicate that the PS particle size has a dramatic decrease when block copolymers are blended with copolymer. And the most effective compatibilizer is the S-b-E block copolymer.

Raman spectrum of the pure PS and HDPE are presented in Fig. 7. It is shown that the Raman band at 1560 and 3044.9 cm^{-1} is suited for visualizing PS, while the 2735.5 cm^{-1} band suited for visualizing HDPE. The peak height, peak ratio and the ratio of half-width at different locations of the blend molding are measured, and the results from four samples are compared and presented in Table 1. Again, the results in the particle size distribution from Raman spectroscopy and micro-TA are also agreement with each other, and S-b-E block copolymer is the most effective compatibilizer.

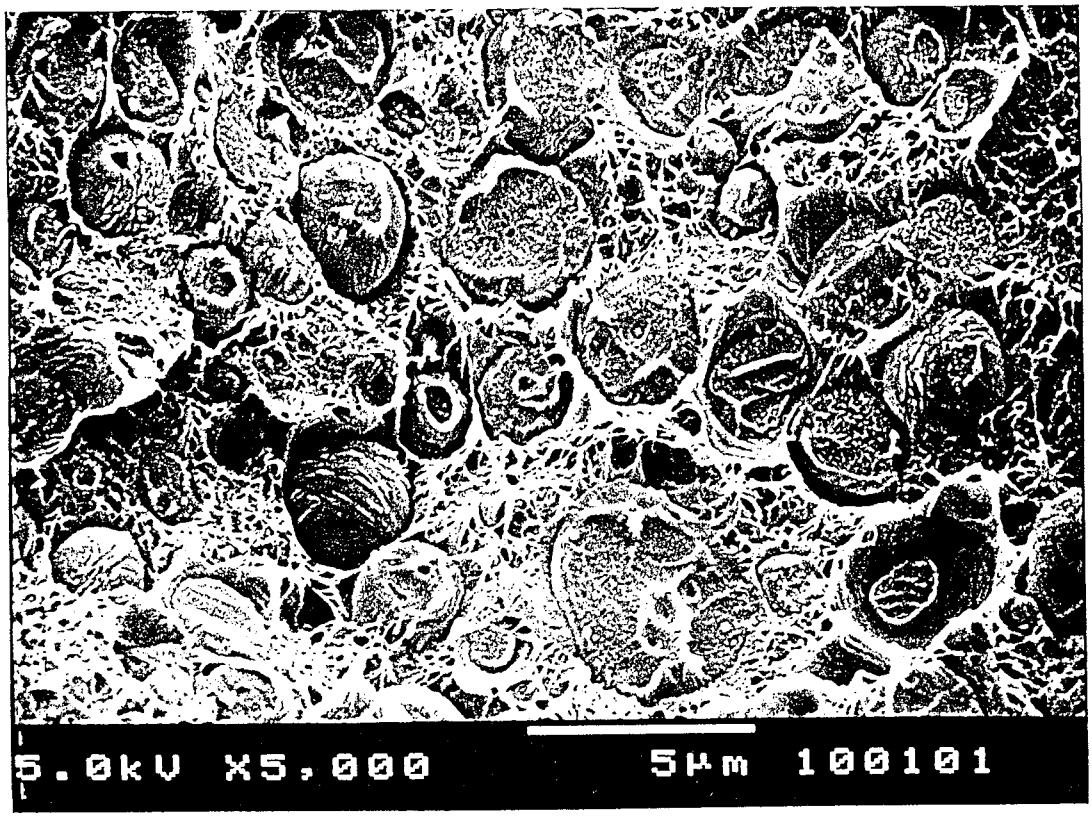

Fig. 5. SEM image of HDPE/PS blend without compatibilizer.

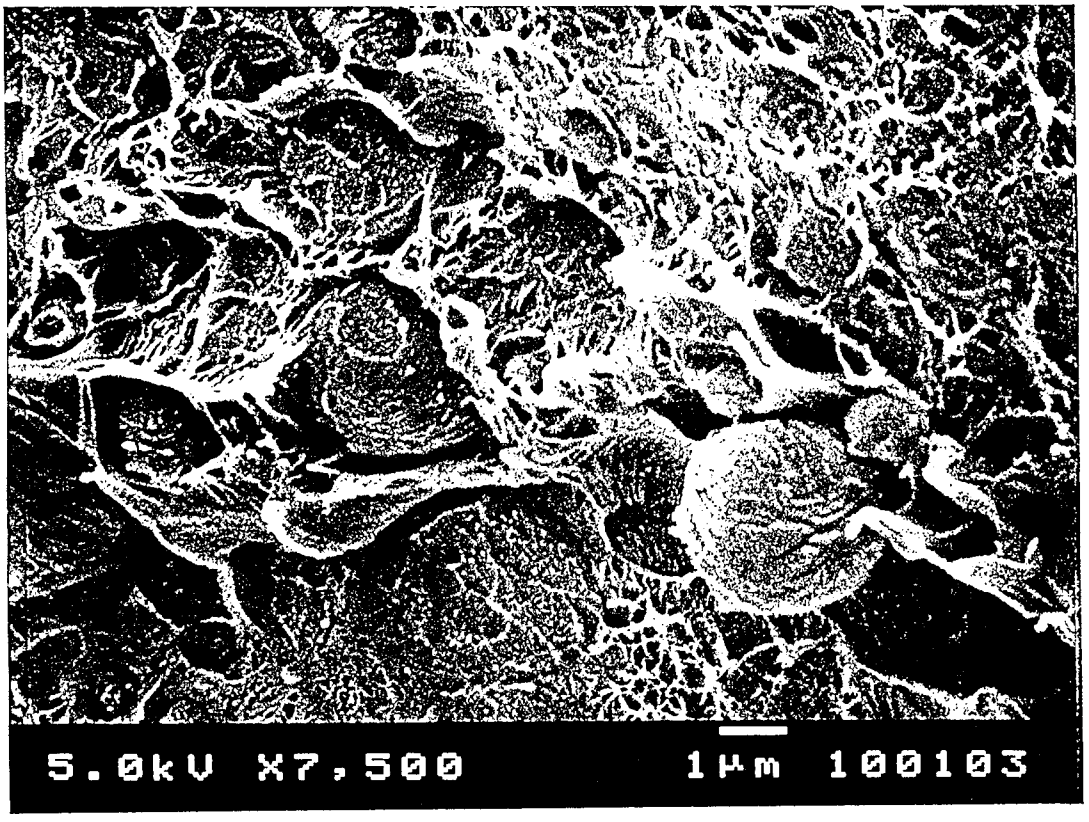

Fig. 6. SEM image of HDPE/PS blend with S–EB–S block polymer.

Table 1
Raman spectroscopy results[a]

Ratio	Item	None	S-EB-S	S-b-EP	S-b-E
1:3	Ratio of half-width	5.3	1.5	1.3	0.7
2:3	Ratio of half-width	2.5	1.0	0.7	0.4

[a] 1 stand for 3044.9 cm^{-1} (PS); 2 stand for 1560.8 cm^{-1} (PS); 3 stand for 2735.5 cm^{-1} (HDPE).

4. Conclusions

1. Micro-TA technique has applied to compare three different mixing methods on high-density polyethylene and polystyrene blend polymer. When a polymer is blended into another one, it is usually dispersed into matrix as small particles. The polystyrene particle size can be readily visualized by micro-TA. The smaller the particle size is, the more homogeneous the blend is. When 2% S-E block copolymers have been added, the average particle sizes have a significant decrease. Micro-TA had been proved to be a powerful technique in the field of materials characterization.
2. Micro-TA shows that an effective compatibilizer can modify the phase morphology and blend component distribution rendering the HDPE/PS blend more homogeneous. The S-b-E block copolymer is the most effective compatibilizer, it can help decrease the domain size of the dispersed polystyrene phase while improving its dispersion in the polyethylene matrix. The results of Raman spectroscopy and SEM are in agreement with the micro-TA result for blend uniformity. Due to the easy sample preparation and experiment operation, micro-TA can serve as a convenient and powerful tool for providing not only detailed information on polymer structure and copolymer composition, but also on polymer

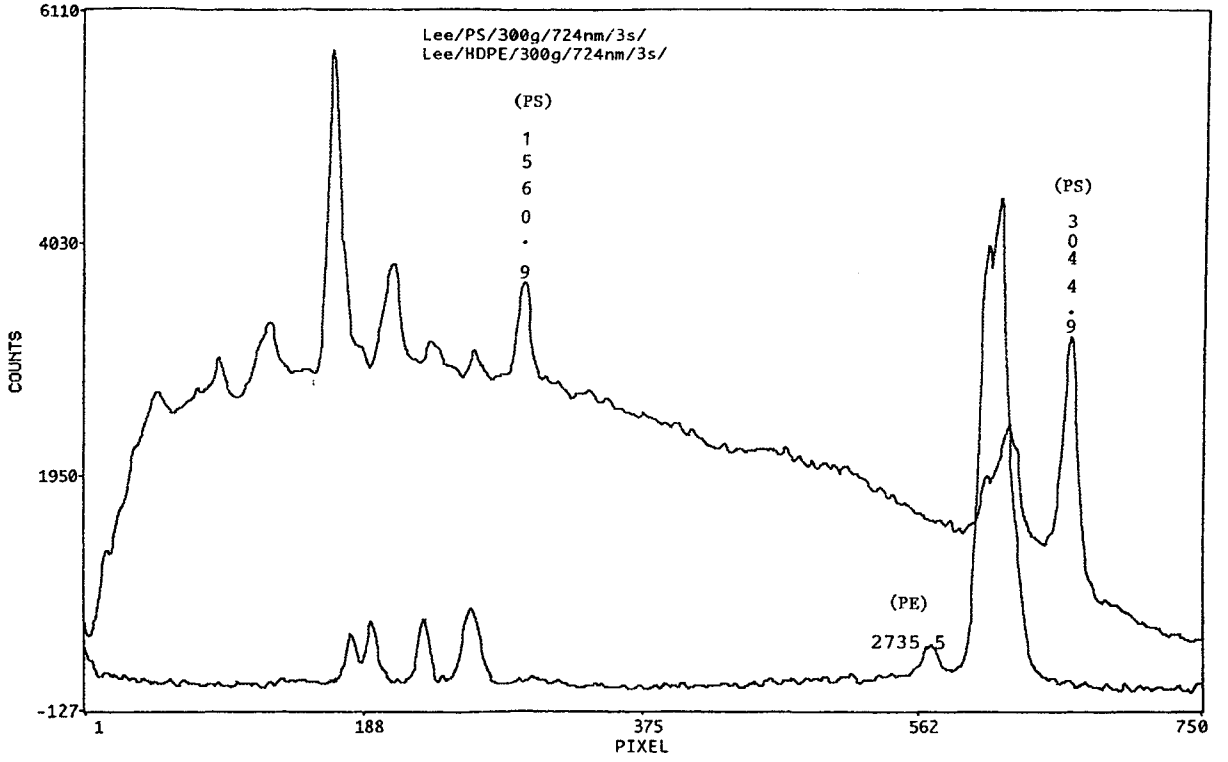

Fig. 7. Raman spectrum of pure HDPE and PS.

blend compatibility in component dispersion and uniformity.

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