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# Fast determination of phase inversion in polymer blends using ultrasonic technique

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## Abstract

Ultrasonic attenuation and velocity, together with SEM observation were used to investigate the morphology of some polymer blends. For miscible polymer blends of PVC/NBR, because there is no phase inversion but a homogeneous system a linear change (without discontinuity) of ultrasonic velocity and attenuation was observed in a whole composition ranges. For immiscible polymer blends, namely, PP/PS, PS/EPDM and PS/SBS system, the non-linear variation of ultrasonic velocity with composition indicates the immiscibility. On the other hand, the intensity of scattering attenuation changed from system to system depending on the size of dispersed phase, but a discontinuity of scattering attenuation was always observed as the phase inversion occurred. Our result suggests the sensitivity of ultrasonic attention vs phase inversion and may be served as a useful method to fast determine the phase inversion for immiscible polymer blends.

*Keywords:* Ultrasonic attenuation; Phase inversion; Discontinuity

## 1. Introduction

Polymer blending has become one of the most interesting means to obtain new materials with specific properties rather than synthesis of new polymer. Some properties can be combined by blending different polymers together, and even be improved in comparison with individual components. It has been well established that the finial properties of polymer blends are directly related to the morphology of polymer blends. For instance, a laminar morphology of the dispersed phase in matrix can achieve good gas barrier property [1,2]; a brittle blend will transit to ductile one when the matrix ligament thickness (inter particle distance) is smaller than a critical matrix ligament thickness ($T_c$) for some polymer blends [3,4]. In immiscible binary blends, it is well established that the morphology can be grouped roughly into: (1) co-continuous morphology and (2) dispersed morphology. Usually the minority forms the dispersed phase and the majority forms the continuous matrix, and the phase inversion takes place as the dispersed phase becomes the major component. Generally, there are three major factors that govern the morphology of immiscible polymer blends. They are: (1) the rheological and interfacial properties of the constituent components (such as, shear viscosity and fluid elasticity, interfacial tension); (2) blend composition; and (3) processing variables (such as temperature, shear rate). In the past, a lot of work has been done on how these three factors determine blend morphology.

Up to now, many techniques have been used to characterize the morphology of polymer blends, which are generally divided into two groups: (1) directly observing the morphology using optical microscopy or electronic microscopy like scanning electron microscopy (SEM) and transmission electron microscopy (TEM); (2) indirectly inferring the morphology by investigating the mechanical relaxation properties of polymer blends, such as the property of glass transition using differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA) et al., or by obtaining the scattering information using scattering techniques like light scattering [5–7], neutron scattering [8,9] and X-ray scattering [10] et al. Ultrasonic technique is also an effective method to investigate the morphology of polymer blends. Hourston and Hughes [11,12] firstly used ultrasonic velocity to investigate the

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compatibility and morphology of polymer blends in solid forms at low frequency (15 kHz). Then Singh and Singh [13,14] reported the use of ultrasonic velocity for compatibility investigation in both solid and solution-blend systems. They found that the ultrasonic velocity varies linearly with composition for compatible blends while velocity deviates from linearity for incompatible blends. The use of ultrasonic attenuation was reported by Shaw and Singh [15] to study the compatibility of PS/EPDM system. In fact, ultrasonic attenuation is more sensitive than velocity to characterize the compatibility and morphology of blends. However, probably due to the complicated attenuation mechanism, few investigations [16] have been reported on the application of ultrasonic attenuation to characterize the compatibility and morphology of polymer blends.

In this article, we report our efforts to investigate the phase morphology in several polymer blends using both ultrasonic attenuation and velocity. We found always a discontinuity of ultrasonic attenuation as the phase inversion occurs for the selected immiscible polymer blends (namely, PS/EPDM, PS/SBS and PP/PS blends), compared with a linear change of ultrasonic attenuation and velocity with composition for miscible polymer blends (no phase inversion occurs, taking PVC/NBR blends as an example). This result suggests that the discontinuity of ultrasonic attenuation may serve as a useful method to fast determine the phase inversion for immiscible polymer blends.

## 2. Experimental

### 2.1. Materials

The polymers used in the experiments are all commercial products. PP (2401, melt flow index is 2.5 g/10 min, and density is 0.91 g/cm$^3$) and PS (666D, melt flow index is 4.3 g/10 min, and density is 1.05 g/cm$^3$) were purchased from Yan Shan Petroleum Chemical, China; SBS (F675, $M_n = 1.8 \times 10^5$, and the styrene content is about 40% with a density of 0.92 g/cm$^3$) was from Mao Ming Petroleum Chemical, China; EPDM (3745P, density is 0.88 g/cm$^3$) was purchased from DoPont Dow Elastomers LLC, USA; PVC (SG-7) was obtained from Shanghai Tianyuan Chemical, China; NBR (acrylonitrile content is 33%) was from Lanzhou Chemical Company, China.

### 2.2. Preparation of samples

#### 2.2.1. The preparation of PS/EPDM, PS/SBS and PVC/NBR specimens

The blending of PS and EPDM in various proportions was first conducted using a internal mixer (Haake90, Shanghai Light Machine Moulding Factory, Shanghai, China) at a rotor speed of 60 rpm for 10 min, and the barrel temperature was controlled at 190 °C. Then the blends were discharged and compressed into 2-mm-thick plate at 190 °C using 0.63 MN Semi-automatic Moulding Press (Shanghai Zimmerli Weili Rubber and Plastic Machinery Co. Ltd, Shanghai, China). The preparation of PS/SBS specimens in various proportions is similar to that of PS/EPDM. However, the preparation of PVC/NBR specimens is a little different. The PVC resin was premixed with 5% by weight of stabilizer using Haake internal mixer at a speed of 40 rpm for 3 min at 185 °C, then the NBR was charged and mixing was performed for another 10 min. In order to reduce the degradation of the samples, the mixing temperature was gradually decreased in accordance with the increasing of NBR composition. The blends were then compressed into 1-mm-thick plate at 180 °C.

#### 2.2.2. The preparation of PP/PS specimens

Various blends were prepared by varying the PS content using a twin-screw extruder (TSSJ-25 co-rotating twin-screw extruder). The barrel temperatures were set at 140/160/190/210/210/195 °C and a screw speed of 120 rpm was used (the mixing time is less than 3 min). The $L/D$ ratio of the screws was 32, and $D = 25$ mm. The filaments obtained upon extrusion were immediately quenched in water, and then cut into pellets by a pelletizer. After compounding, the blends were injection moulded into disc-shaped specimen using a PS40E5ASE injection-moulding machine. The temperature was chosen as 210/210/190/175 °C from die to hopper. The temperature of the mold was kept at room temperature.

### 2.3. SEM observation

The morphologies of blends were studied using JSM-5900LV scanning electron microscopy operated at 20 kV. The samples were fractured first in liquid nitrogen and one component of these blends was selectively etched by proper solvent to enhance the contrast. Then the etched surfaces were sputter-coated with a thin layer. The solvents as well as corresponding etching time are listed in Table 1.

### 2.4. Ultrasonic detection

#### 2.4.1. Ultrasonics principle

Ultrasound is a kind of mechanical wave whose frequency is more than 20 kHz. Ultrasound can be generated from the periodically vibrating piezoelectric transducer and propagate in viscoelastic polymers. Ultrasonically, there are

Table 1
The samples versus corresponding etching solvents, etched component and etching time

| Sample | Etching solvent | Etched component | Etching time |
|---|---|---|---|
| PS/EPDM | Acetone | PS | 10 min |
| PS/SBS | Heptane | SBS | 2 h |
| PP/PS | Toluene | PS | 2 h |

four types of waves including longitudinal wave, shear wave, Rayleigh wave and Lamb wave. However, longitudinal wave is often preferentially utilized to characterize the properties of materials. The velocity and attenuation of longitudinal wave in certain material are two useful physical parameters to explore material properties. Theoretically, the velocity of longitudinal wave $v$ in solid is related to material's density $\rho$, Young's modulus $E$ and Poisson's ratio $\sigma$, which is given as:

$$v = \sqrt{\frac{E(1-\sigma)}{\rho(1+\sigma)(1-\sigma)}} \tag{1}$$

Therefore, different Young's modulus and density can result in different velocity. The attenuation refers to the phenomenon that ultrasonic energy decreases with wave propagation in material, which arises mainly from three causes: (1) spread of sonic beam; (2) scattering in inhomogeneous materials; (3) absorption by material including internal friction (viscosity), thermoelastic absorption, phonon–phonon interactions. In our work, each group of polymer blends is molded into plate with the same thickness. So, the attenuation arising from spread of sonic beam can be neglected systemically.

### 2.4.2. Ultrasonic system and method of detection

The ultrasonic system comprises of a 5-MHz longitudinal wave pulsing/receiving transducer (5P6) and a PCUS10 card inserted in the mainboard of a computer, which consists of all the components involved in ultrasonic equipment like frequency generator, wave filter, A/D converter, data processor etc. The sampling rate is 80 Ms/s. The ultrasonic analysis system is supported by MESUS software.

The ultrasonic measurement was performed using pulse-echo technique. As shown in Fig. 1, the incident wave is generated from the transducer contacting directly with the plate specimen by putting coupling agent of glycerin, and transmitted in the sample of thickness $X$, reflected back and forth at the two surfaces. When the reflected wave reaches the upper surface and is received by the transducer, an echo signal containing several oscillations will be gained. A series of echo signals can be obtained as the ultrasound is reflected between the two surfaces, however, the amplitudes of the echo signals are gradually decreased with time for ultrasonic attenuation, as is showed in Fig. 2. In our experiments, the first two echo signals, whose amplitudes ($A1$, $A2$) and corresponding time ($t1$, $t2$) can be read after demodulation (Fig. 3), are chosen to calculate the velocity $v$ and attenuation $\alpha$.

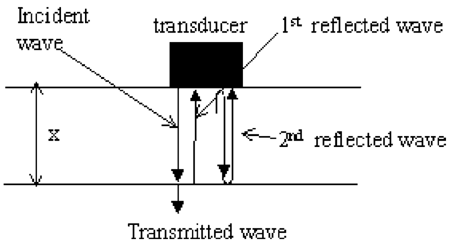

Fig. 1. Schematic representation of ultrasound propagation.

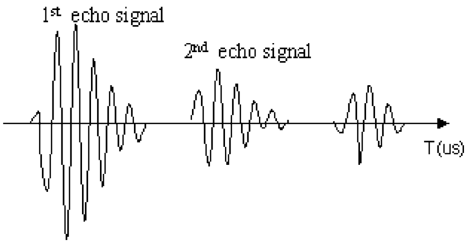

Fig. 2. Echo signals of ultrasound.

$$v = \frac{2X}{t2 - t1} \tag{2}$$

$$\alpha = \frac{20\log_{10}(A1/A2)}{2X} \tag{3}$$

## 3. Results

### 3.1. PP/PS blends

We begin with PP/PS system because it serves as a typical example for immiscible polymer blends and was studied extensively in the past. PP and PS are two of the most widely used plastics in the world. In this system, one is crystalline phase and the other is amorphous phase. A lot of work has been done on the morphology and mechanical properties of PP/PS blends [17–23]. Sung-Goo Lee [24] reported that when the melt viscosity of PS was higher than that of PP, there was a phase inversion at the PS composition of around 75 wt% in PP/PS blends. Fig. 4 shows the change of morphology of samples as a function of composition for PP/PS studied in our experiment. The black domains indicate the position of the extracted PS phase. One observes a sea-island structure in the composition up to 46% PS by volume, which indicates that PS forms a dispersed phase and PP forms a continuous phase in the composition region. The shape of PS dispersed phase is

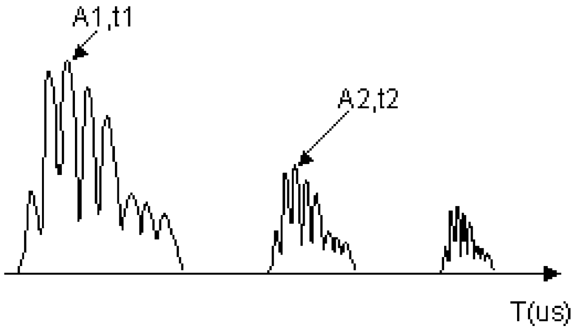

Fig. 3. Echo signals after demodulation.

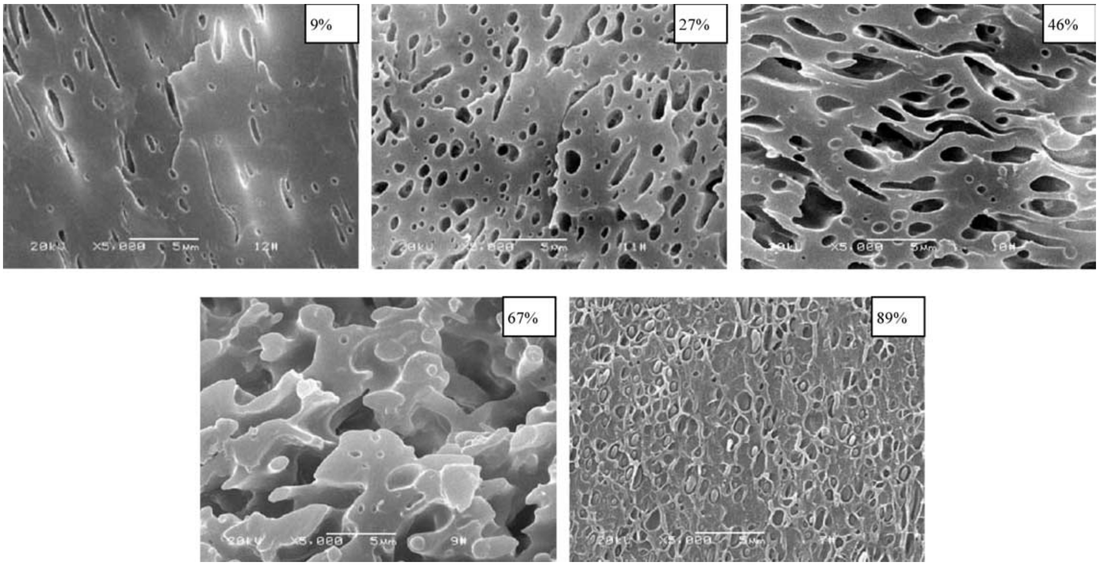

Fig. 4. Scanning electron micrographs of PP/PS blends. The number in each graph refers to the vol% of PS in PP/PS blends.

elongated spherical and the size of PS increases from 0.5–1.0 to 2.0–3.0 μm when PS content increases from 9 to 46% by volume. The phase inversion takes place at 67% by volume of PS where co-continuous morphology is seen. The variation of ultrasonic attenuation with composition in Fig. 5 takes on non-linear relation: Linear decrease first up to 57% PS content, and then the inflexion of this curve occurs just at 67% of PS where phase inversion takes place, as indicated by SEM observation in Fig. 4. In addition, the inverted S-shaped curve of ultrasonic velocity versus composition in Fig. 6 indicates the overall immiscibility, in good agreement with literature.

Our result is exciting, which suggests the sensitivity of the ultrasonic attenuation related to phase morphology in PP/PS blends. The discontinuity of ultrasonic attenuation with composition may be used as fast determination of phase inversion for immiscible polymer blends. To verify this observation, one has to check other polymer blends. Following we will discuss the results obtained in PS/EPDM blends and PS/SBS blends.

### 3.2. PS/EPDM and PS/SBS system

It is known that EPDM rubber is immiscible with PS over the entire range of concentrations [25]. As is apparently shown in Fig. 7, below 46% by volume of PS, PS forms the dispersed phase while EPDM rubber forms the continuous matrix. In addition, the particle size of PS phase increases with the increasing of PS content. The phase inversion occurs at about 56% of PS, then EPDM rubber forms the dispersed phase and PS becomes the matrix. It is shown in Fig. 8 that the attenuation increases steadily with PS content before 36% by volume, but after that, there is a dramatic rise in attenuation till to 56% of PS. However, the strongest attenuation at 56% of PS can not be quantified with the present measure system due to insufficient signal-to-noise

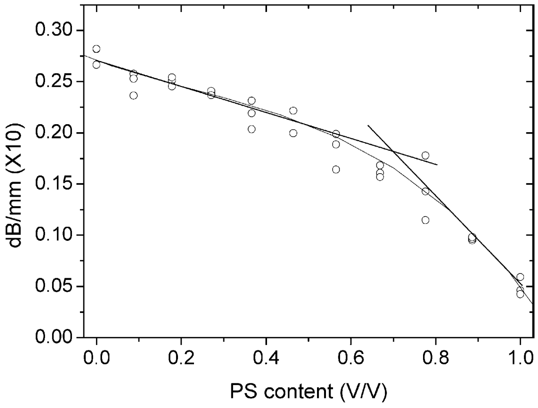

Fig. 5. Variation of ultrasonic attenuation with volume fraction of PS in PP/PS blends.

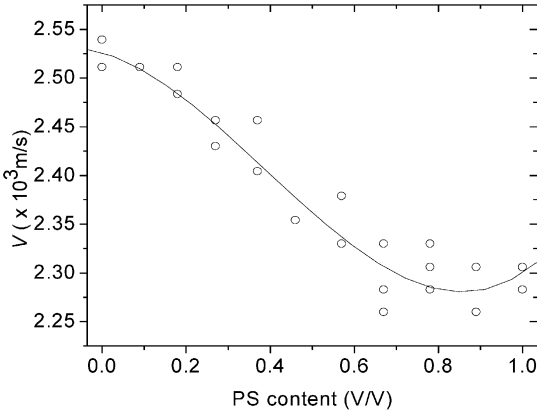

Fig. 6. Variation of ultrasonic velocity with volume fraction of PS in PP/PS blends.

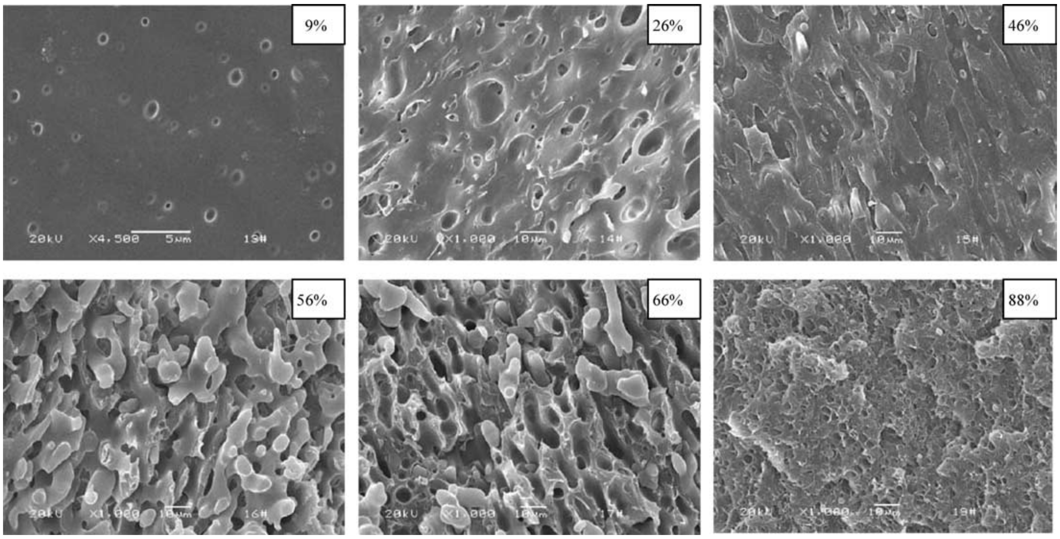

Fig. 7. Scanning electron micrographs of PS/EPDM blends. The number in each graph refers to the vol% of PS in PS/EPDM blends.

ratio of reflected waves. After 56% of PS, the attenuation drops sharply again. Fig. 10 shows the relation between ultrasonic velocity and composition, from which it can be seen that the non-linear behavior indicates the multi-phase nature of PS/EPDM system, and the inflexion occurring at around 53% of PS just corresponding to the phase inversion.

In PS/SBS blends, one expects certain miscibility between PS and SBS due to the polystyrene blocks in SBS chain. However, as can be seen from Fig. 11, the system exhibits a certain two-phase morphology, and the phase inversion occurs at about 60% by volume of PS. But compared with PS/EPDM system, the sizes of dispersed phase particles in PS/SBS system are much smaller and not more than 1 μm. Fig. 12 shows the variation of ultrasonic attenuation with composition. It can be seen that below 60% of PS, the attenuation keeps unchanged, but after that point it drops sharply. Fig. 14 shows the variation of velocity with composition. It can be seen that the inflexion occurs also at 60% of PS.

In summary, here we see the other two examples that the phase morphology in immiscible polymer blends can be well related to the change of ultrasonic attenuation. Once the phase inversion occurs, one always observes a discontinuity of ultrasonic attenuation. If so, one should observe a linear change (without discontinuity) of ultrasonic attenuation in whole composition ranges for miscible polymer blends, since there is no phase inversion but a homogeneous system. For this purpose, we extended our work further to PVC/NBR blends, a typical example for miscible polymer blends.

### 3.3. PVC/NBR system

It is well known that the miscibility of PVC/NBR blends varies with the acrylonitrile content in NBR, and PVC is miscible with NBR with 23–45% acrylonitrile content at all composition ranges [26]. In our experiment, to obtain high miscibility, 33%-acrylonitrile-content NBR was chosen to blend with PVC. Fig. 15 shows the variation of ultrasonic

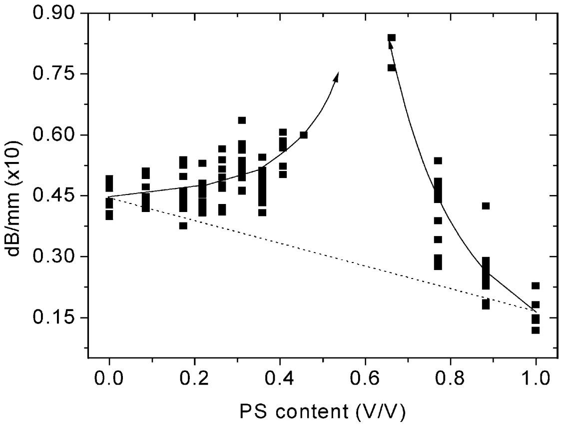

Fig. 8. Variation of ultrasonic attenuation with volume fraction of PS in PS/EPDM blends.

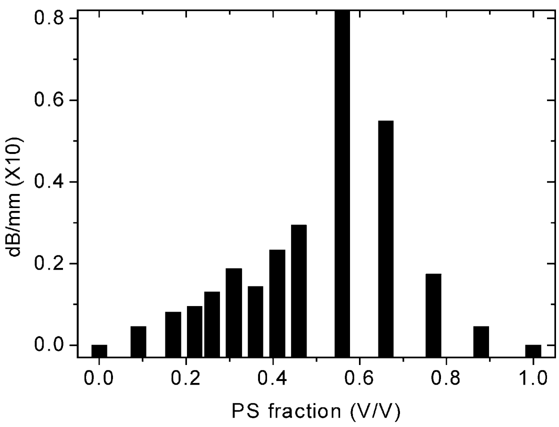

Fig. 9. Variation of attenuation induced by scattering loss with volume fraction of PS in PS/EPDM blends.

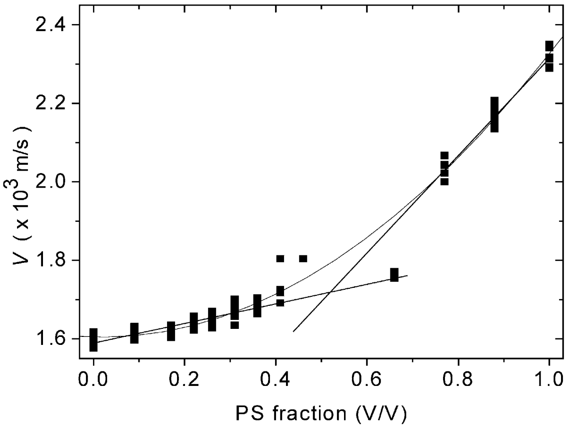

Fig. 10. Variation of ultrasonic velocity with volume fraction of PS in PS/EPDM blends.

attenuation with PVC content. The linear relation between ultrasonic attenuation and composition indicates that little scattering loss contributes to ultrasonic attenuation according to Takayanagi's model [27] (Eq. (6) below). That is to say, the blends are homogeneous and no phase inversion occurs in this system. Meanwhile, the linear variation of ultrasonic velocity with composition is also observed in Fig. 16 at all composition ranges for the miscible blends, just in agreement with our expectation.

## 4. Discussions

Ultrasonic velocity was used to study the miscibility or compatibility of multi-phase system in the past. It provides a fast and non-damaged method for investigation of polymer phase morphology. Here we find that ultrasonic attenuation seems to be more sensitive to the phase inversion. There are many factors, which will give rise to ultrasonic attenuation.

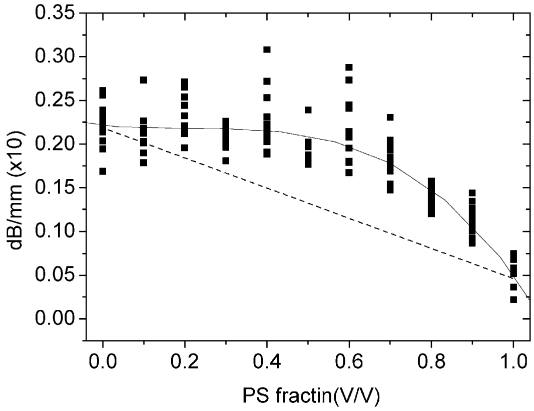

Fig. 12. Variation of ultrasonic attenuation with volume fraction of PS in PS/SBS blends.

However, as far as heterogeneous blends are concerned, viscoelastic absorption loss and scattering loss play a major role in ultrasonic attenuation. Beltzer and Brauner [28] put forward a theoretical model of wave attenuation in viscoelastic composites based on independent scattering assumption, that is, the spatial decay of the time-averaged energy flux density $\langle e \rangle$ of the plane wave propagating into the $x_1$-direction is assumed in the form

$$\frac{\mathrm{d}\langle e \rangle}{\mathrm{d}x_1} = -\langle I^{\mathrm{sca}} \rangle - \langle I^{\mathrm{abs}} \rangle - \langle I^{\mathrm{mat}} \rangle \tag{4}$$

where $\langle I^{\mathrm{sca}} \rangle$, $\langle I^{\mathrm{abs}} \rangle$ and $\langle I^{\mathrm{mat}} \rangle$ are the scattering loss rate, the absorption loss rate in the particles and the absorption loss rate in the matrix, respectively. And they further urged that when the dispersed particles are elastic, they do not contribute to absorption loss. In these systems studied in our work, all dispersed particles are viscoelastic, therefore, they may contribute to ultrasonic attenuation owing to absorption loss.

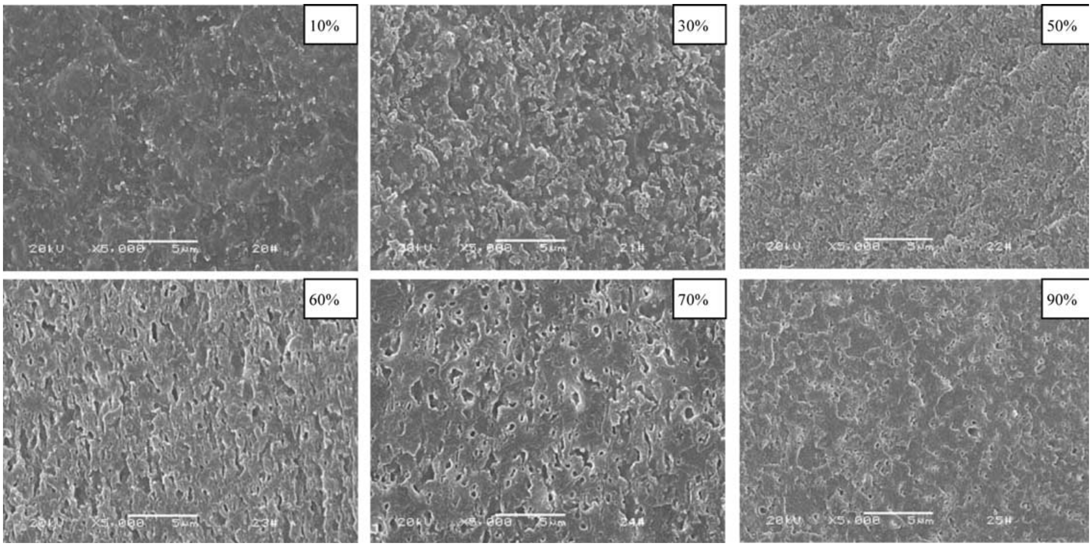

Fig. 11. Scanning electron micrographs of PS/SBS blends. The number in each graph refers to the vol% of PS in PS/SBS blends.

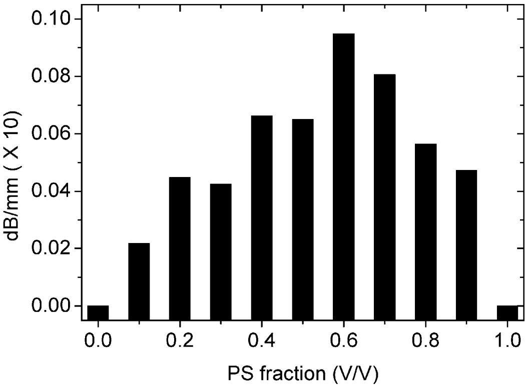

Fig. 13. Variation of attenuation induced by scattering loss with volume fraction of PS in PS/SBS blends.

In immiscible blends, the dispersed phase and the matrix have different density and stiffness, consequently, scattering loss is excepted to occur and accounts for some portion of the wave attenuation, especially, when the particle diameter is of the same order of magnitude as the wave length of ultrasound. Okano [29] assumed a formulation describing the scattering attenuation in the case where spherical domains 2 with radius $\alpha$ are dispersed in continuous matrix 1,

$$\alpha_s = \frac{8\pi^4 a^3}{\lambda^4}\left[\frac{1}{3}\left(\frac{K_1 - K_2}{K_1}\right)^2 + \left(\frac{\rho_1 - \rho_2}{2\rho_2 + \rho_1}\right)^2\right]\phi \qquad (5)$$

where $\lambda$, $K$, $\rho$, $\phi$ are the wave length, the bulk modulus, the density and the volume fraction of dispersed phase, respectively. It can be deduced from this formulation that the scattering attenuation increases with the increasing of particle radius and volume fraction of dispersed phase. One also expects a sharp change of the scattering attenuation as the phase inversion takes place, where individuals particles are connected together to a continuous phase.

According to Beltzer and Brauner's model [28], both dispersed phase and matrix contribute to absorption loss of wave energy. The absorption loss mainly results from the internal friction occurring in the process of Brownian motions of polymer segments induced by ultrasound. In our experiments, taking PS/EPDM blends as an example, the PS in glassy state has lower internal friction than the EPDM in rubbery state, so the absorption loss in pure PS should be lower than in pure EPDM, which is verified at 0 and 100% by volume of PS in Fig. 8. Takayanagi et al. [27] proposed a model which was modified later by Gary and McCrum [30] to investigate the compatibility of multi-component system, and recently Youssef [16] successfully used this model to predict the compatibility of two-components system. According to the model, the ultrasonic attenuation can be calculated from the attenuation of each component,

$$\alpha = w_1\alpha_1 + w_2\alpha_2 \qquad (6)$$

where $w_1$ and $w_2$ denote the weight fraction of component 1 and 2, respectively. Herein, coincidence of $\alpha$ with experimental attenuation value would indicate the compatibility of this system. This model implicates that in homogeneous system, there is no scattering loss and the total attenuation is the combination of adsorption loss of each component. Therefore, in order to observe more clearly the relation of scattering loss with composition in PS/EPDM system, the scattering loss value is obtained through

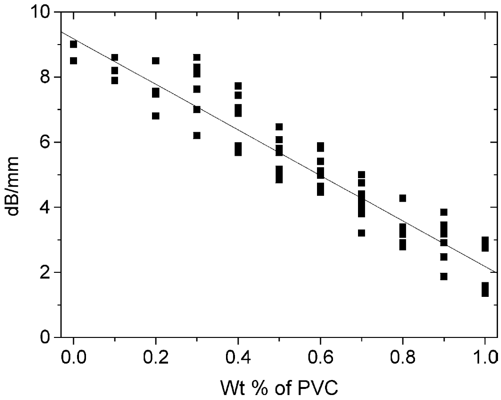

Fig. 15. Variation of ultrasonic attenuation with wt% of PVC in PVC/NBR blends.

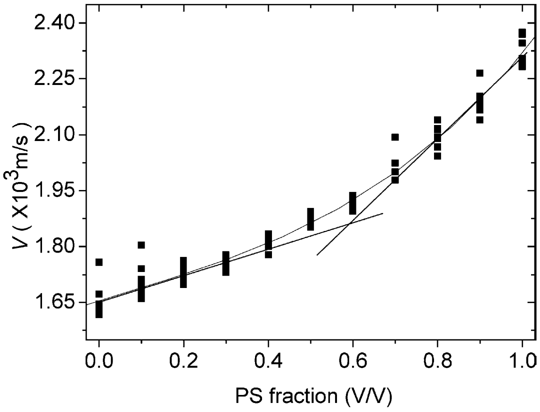

Fig. 14. Variation of ultrasonic velocity with volume fraction of PS in PS/SBS blends.

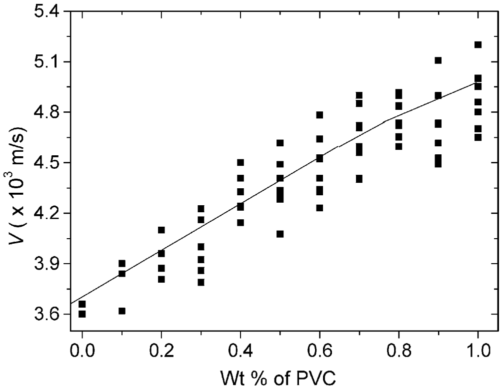

Fig. 16. Variation of ultrasonic velocity with wt% of PVC in PVC/NBR blends.

subtracting absorption loss from the total attenuation. The dash line in Fig. 8 shows the variation of absorption loss with volume fraction of PS according to Eq. (6) by replacing weight fraction with volume fraction, and Fig. 9 gives the scattering attenuation as a function of PS content. It can be seen from Fig. 9 that the maximum of scattering attenuation occurs at 56% by volume of PS, where the phase inversion takes place. Comparing Figs. 7 and 9 shows that the rise in scattering attenuation corresponds to the increase in sizes of dispersed phase particles and the maximum at 56% of PS corresponds to the co-continuous morphology. Similar to PS/EPDM system, scattering attenuation of PS/SBS system can also be obtained through subtracting absorption loss from the total attenuation of this system, which is shown in Fig. 13. The maximum of scattering attenuation occurs at 60% by volume of PS, where the phase inversion takes place. Compared with Fig. 9, the variation of scattering attenuation with composition is moderate. The largest scattering attenuation value, roughly $0.09 \times 10$ dB/mm, is much smaller than that in Fig. 9. It verifies that scattering attenuation in PS/SBS system is much less than that in PS/EPDM system due to higher miscibility resulting in smaller dispersed phase particles in PS/SBS system.

## 5. Conclusion

In summary, both ultrasonic attenuation and velocity are sensitive to the miscibility and morphology of polymer blends. Particularly, we observed always a discontinuity of scattering attenuation as the phase inversion occurs for immiscible polymer blends of PP/PS, PS/EPDM and PS/SBS, and a linear change of scattering attenuation in the whole composition ranges for miscible polymer blends of PVC/NBR. If our work can be extended to other polymer blends, this will serve a useful method to fast determine the phase inversion for immiscible polymer blends.

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