Acoustic Analysis of Composite Soft Materials. I. Characterization of the Core and Boundary Layer from Compressibility of Core/Shell Particles Dispersed in Poly(vinyl chloride)

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ABSTRACT: The sound velocity of butyl acrylate rubber particles modified by poly(methyl methacrylate) in poly(vinyl chloride) was measured as a function of particle concentration. A model for estimating the adiabatic compressibility of the particle and the boundary layer was proposed. From the model, the partial specific adiabatic compressibility of the particles and the rubber core were evaluated. The adiabatic compressibility of the rubber core was estimated as 3.82×10^{-10} Pa^{-1}. The adiabatic compressibility of the poly(methyl methacrylate) shell is discussed based on the modified model. The study indicates that the shell, including the boundary layer between butyl rubber and poly(methyl methacrylate), is perturbed by the butyl acrylate molecules and is so soft as to be comparable to the rubber. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 2089–2094, 2001

Key words: core/shell particle; poly(vinyl chloride); poly(methyl methacrylate); adiabatic compressibility; sound velocity

INTRODUCTION

The physical properties of composite soft materials have been evaluated by various methods.[1,2] Macroscopic properties, such as the rheological, thermal, and mechanical properties of materials, are important for practical usage. Molecular structure has been investigated by means of X-ray, IR, Raman scattering measurements, and so on. To enable further improvement of composite polymers or design of new functional materials, it is desirable to obtain information regarding properties and morphology on the microscopic scale, between the molecular and the macroscopic.

The acoustic method has several advantages in material characterization. The longitudinal, shear, bulk, and Young's moduli are evaluated from the longitudinal and transverse sound velocity and the density data. The velocity can be obtained with a high degree of accuracy, and is sensitive to subtle changes in the local structure and properties of materials. Thus, sound velocity measurement is a useful method for characterizing soft materials and has been used to investigate the physical properties of solid polymers.[3–8] Morphology can be studied on the micrometer scale by means of scanning acoustic microscopy. In addition, acoustic material characterization is performed under noncontact and nondestructive conditions. Our final goal is to characterize, using acoustic methods, composite soft materials composed of polymers, and to interpret their macroscopic properties from microscopic levels.

In polymer and colloidal solutions, the partial specific adiabatic compressibility of the solutes is interpreted well by the solvated model proposed by

Nomura and Miyahara.[9,10] The model gives information about not only the solute itself but also, with appropriate assumptions, the solvation layer.

As amorphous polymers are considered to be homogeneous, composite materials that are composed of amorphous polymer and dispersed particles are regarded as forms of colloidal solution. That is, the polymer matrix and the dispersed particles are regarded as the solvent and solute, respectively, and the interface or boundary layer between the particles and matrix polymer corresponds to the solvation layer. Application of the solvation model to composite materials based on the analogy described above makes it possible to estimate the partial specific adiabatic compressibility of dispersed particles in polymers. In addition, information about the boundary layers or interface will be obtainable.

Rubber particles, glass fiber, or compounds are added to polymers in order to reinforce or cultivate them.[1,2] Rubber particles consisting of a crosslinked rubber core and copolymerized shell are sometimes used to toughen plastics.[11] The bulk properties and morphology of polymers containing core/shell particles have been investigated by several researchers.[12–18] In composite materials, the physical properties of the toughened plastics depend on the nature of the additives and their content. In addition, the mechanical strength of the composite materials is influenced by the dissolved or dispersed states of additives and the boundary layer between the additives and polymers. It is very important to know the properties of the dispersed particles and boundary layer in composite materials.

In this work, we apply a theoretical treatment to obtain the partial specific adiabatic compressibility of particles dispersed in polymer, and apply the theory to core/shell particles dispersed in polymer. The adiabatic compressibility of particle and core are evaluated by extending the above theory. It will be shown that partial specific adiabatic compressibility is useful for studying core/shell particles in polymer.

EXPERIMENTAL

Samples

A composite polymer consists of a polymer matrix of poly(vinyl chloride) (PVC) and butyl acrylate rubber particles (BA). The surfaces of the BA rubber particles are copolymerized by methyl methacrylate (MMA) in order to enhance the com-

Table I   Samples

Sample No.	Ratio of Shell to Core (wt %)	Particle Diameter ($\times 10^{-7}$ m)	Core Diameter ($\times 10^{-7}$ m)	Thickness ($\times 10^{-7}$ m)
1	5	1.69	1.66	0.028
2	10	1.68	1.62	0.058
3	15	1.65	1.56	0.087
4	20	1.59	1.49	0.112

patibility of the rubber particles. In other words, the rubber particles comprise cores of BA rubber and poly(methyl methacrylate) (PMMA)-rich shells. All samples used here were supplied by Kaneka Chemicals Co. Ltd. The diameter of the core and the % weight of the core and shell are summarized in Table I.

Sound Velocity and Density Measurements

Sound velocity was obtained from measurement of the time required for transmission through a sample of thickness l. A sample with a cross section of 4 cm^2 and a thickness of 2–3 mm was prepared for the measurement. The transmit time t was measured by the TAC (time-to-amplitude converter) method. Lead zirconate titanate (PZT) and X-cut quartz operating at 5 MHz were used as transducers for the transverse and longitudinal sound waves, respectively. The sound velocity V is calculated from the following equation:

$$V = l/t \tag{1}$$

Experimental error for sound velocity was within 3 ms^{-1}. Details of the apparatus and experimental method are given in a previous paper.[8]

The adiabatic compressibility κ_s is evaluated from the bulk modulus K.

$$\kappa_s = 1/K \tag{2}$$

where

$$K = M - 4/3G. \tag{3}$$

The longitudinal modulus M and shear modulus G were obtained from the following equations:

$$M = dV_l^2 \tag{4}$$
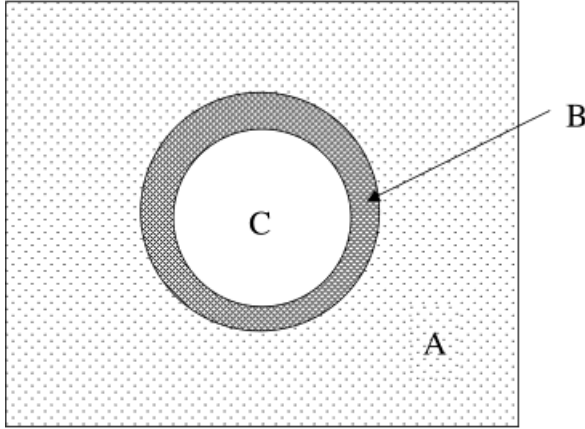
$$G = dV_t^2 \tag{5}$$

Figure 1 Model of composite materials to estimate partial specific compressibility. (A) Matrix, (b) boundary layer, and (C) dispersed particle.

where V_l and V_t are the longitudinal and transverse sound velocities, and d the density. The density of the sample was measured by a pycnometer with a volume of 50 mL. All measurements were carried out at $30 \pm 0.1°C$.

THEORY

When additives are dispersed in polymer, a boundary layer is formed around the additive. From an analogy between solutions and composite materials, the dispersion particles, boundary layer, and matrix correspond to solute, solvation layer, and solvent in solution, respectively. The correspondence is particularly good if the polymer matrix is homogeneous. A composite material consisting of additives and polymer is shown schematically in Figure 1. If the additivity for volumes holds, the volume of the composite polymer is given by the following equation[9,10]:

$$V = (n_m - n_{SM}n_p)v_m + n_p(v_p + n_{SM}v_{SM}) \quad (6)$$

where v_m, v_p, and v_{SM} are the specific volumes of the matrix polymer, the dispersed particles, and the boundary layer, respectively. The n_m and n_p are the gram of the matrix polymer and the dispersion particles, and n_{SM} the gram of the boundary layer per gram of the dispersion particles. The partial specific volume of the dispersion particles is obtained as the derivative of eq. (6) by n_p.

$$\bar{v}_p = v_p + n_{SM}(v_{SM} - v_m) \quad (7)$$

The limiting partial specific compressibility of the dispersion particles is defined by

$$\bar{\kappa}_p^0 = -\frac{1}{\bar{v}_p^0}\left(\frac{\partial \bar{v}_p}{\partial p}\right)_{s,0} \quad (8)$$

The subscript zero refers to the value where the concentration of dispersion particles approaches zero. The letters S and P means entropy and pressure, respectively. From eqs. (7) and (8), the following equation is derived:

$$\bar{\kappa}_p^0 = \frac{v_p}{\bar{v}_p^0}\kappa_p + \frac{n_{SM}}{\bar{v}_p^0}(v_{SM}\kappa_{SM} - v_m\kappa_m) \quad (9)$$

where κ_p, κ_{SM}, and κ_m are the adiabatic compressibility of the particles, the boundary layer, and matrix phase, respectively. If $v_p = \bar{v}_p^0$ is assumed, the first term in the above equation gives the adiabatic compressibility of the particles. In general, the assumption is valid because the difference between v_p and $\bar{v}_p^0$ is small. The second term involves information about the boundary layer and the matrix polymer.

The partial specific volume and adiabatic compressibility are obtained experimentally from the following equations[9,10]:

$$\bar{v}_p^0 = \lim_{x \to 0}\left(1 - \frac{d - x}{d_m}\right)\frac{1}{x} \quad (10)$$

$$\bar{\kappa}_p^0 = -\frac{\kappa_m}{\bar{v}_2^0}\lim_{x \to 0}\left(\frac{d - x}{d_m} - \frac{\kappa}{\kappa_m}\right)\frac{1}{x} \quad (11)$$

where x is the concentration of the dispersed particles (g cm^{-3}). The d and κ are density and adiabatic compressibility of the composite polymer at the concentration of x, respectively.

RESULTS

The longitudinal and transverse sound velocities are plotted against the concentration of dispersed particles in Figures 2 and 3, respectively. The sound velocity decreases as the core/shell particle content increases. The sound velocity extrapolated to zero particle concentration gives that of PVC itself and the values are summarized in Table II. A slight change in extrapolated sound velocity is recognized, depending on the core/shell ratio. The change in the sound velocity of PVC matrix may be caused by preparation conditions

and other factors. In the calculation of for PVC matrix, the extrapolated sound velocity is used.

The representative plot of $[1 - (d - x)/d_m]$ and $[(d - x)/d_m - \kappa/\kappa_m]$ against the concentration of core/shell particles (x) is given in Figure 4. The values of $[1 - (d - x)/d_m]$ and $[(d - x)/d_m - \kappa/\kappa_m]$ are linearly proportional to the particle concentration. The partial specific volume and adiabatic compressibility are estimated from the slope in Figure 4 with eqs. (10) and (11). These results are summarized in Table II together with the density and sound velocity of polymer matrix.

The partial specific volume of a particle is around 1.1 cm^3/g. The specific volume of PMMA estimated from the density is 0.86. As a particle mainly consists of its rubber core, the rubber core contributes to the partial specific volume of the particle.

DISCUSSION

Figure 5 plots the partial specific adiabatic compressibility of a particle against the % wt of
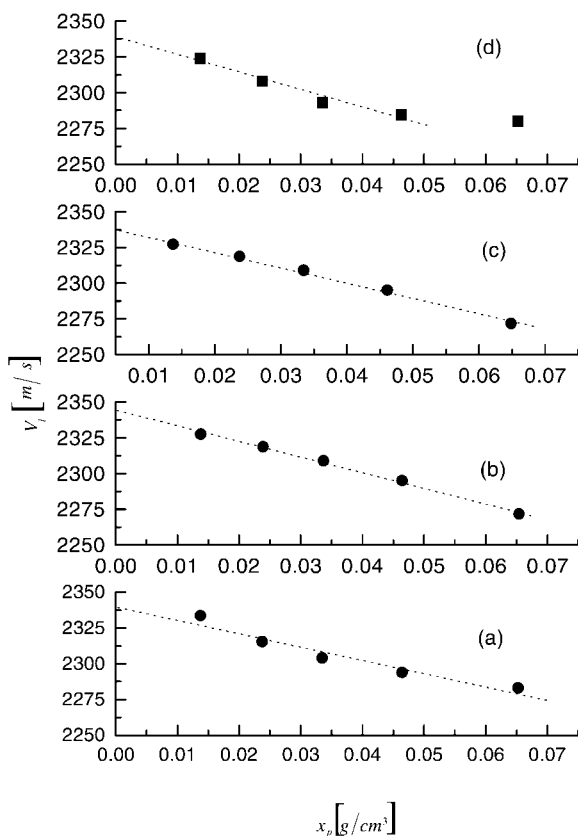

Figure 2 Concentration dependence of longitudinal sound velocity for particle of size 0.17 μm. Ratio of shell/core: (a) 5:95, (b) 10:90, (c) 15:75, and (d) 20:80.
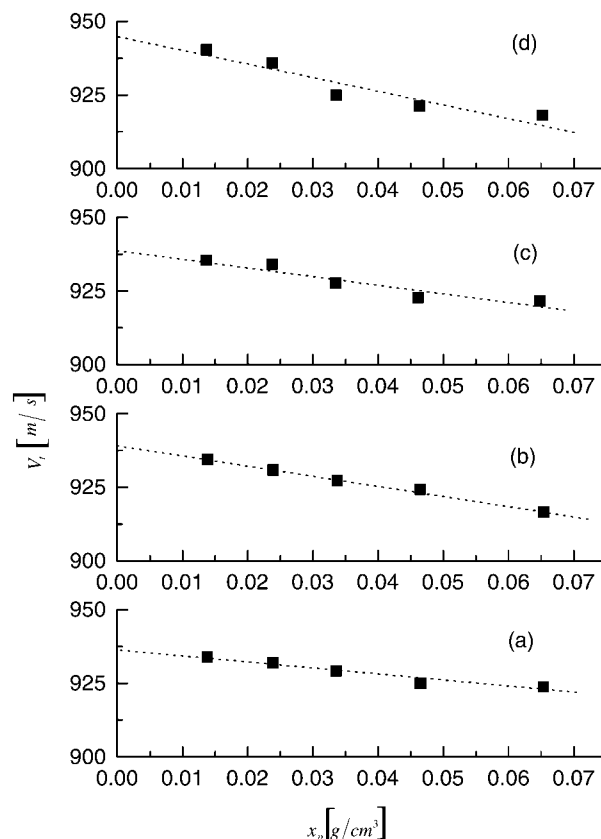

Figure 3 Concentration dependence of transverse sound velocity for a particle of size 0.17 μm. Ratio of shell/core: (a) 5:95, (b) 10:90, (c) 15:75, and (d) 20:80.

PMMA. Weak concentration dependence of partial specific adiabatic compressibility is observed. As the thickness of the shell is of negligible thinness for the core diameter of the samples indicated in Table I, the partial specific adiabatic compressibility in the low content of PMMA is mainly attributable to butyl acrylate rubber. Strictly speaking, the limiting value of the partial specific adiabatic compressibility at the zero concentration of PMMA gives the adiabatic compressibility of rubber itself. The adiabatic compressibility of butyl acrylate rubber is estimated as $\kappa = 3.85 \times 10^{-10}$ Pa^{-1} with = 1.1 and = 1.0 cm^3 g^{-1}. Unfortunately, the adiabatic compressibility of butyl acrylate rubber is unavailable. The adiabatic compressibility of a peroxide-linked latex rubber reported by Wood and Martin[19] is around 4×10^{-10} Pa^{-1} at 30°C. The magnitude of the adiabatic compressibility of butyl acrylate rubber in the core/shell particle is of the same order as natural rubber.

The slight increase in sound velocity should be interpreted from the first and/or second term in eq. (9). The second term is determined by the

Table II   The Density, Longitudinal and Transverse Sound Velocity, and Adiabatic Compressibility of PVC Matrix, and Specific Volume and Specific Adiabatic Compressibility of Core/Shell Particles Dispersed in PVC

Sample No.	d_0 g/cm^3	V_l m/s	V_t m/s	κ_m $\times 10^9$ pa^{-1}	$\bar{v}_p^0$ cm^3/g	$\bar{\kappa}_p^0$ $\times 10^9$ pa^{-1}	$\bar{\kappa}_r^0$ $\times 10^9$ pa^{-1}
1	1.452	2341	937	1.598	1.13	3.53	3.57
2	1.460	2343	938	1.587	1.20	3.55	3.67
3	1.445	2338	939	1.613	1.15	3.58	3.77
4	1.440	2338	944	1.623	1.01	3.64	3.96

properties of the intermediate phase between the shell and the PVC matrix. Although Albert et al. said that PVC and PMMA may be not homogeneously mixed at the molecular level,[20] PMMA is highly compatible with PVC.[21,22] In a previous paper,[22] it was found that the addition of a small amount of PMMA to bulk PVC does not affect the bulk modulus of the PVC. This means that the phase between the PMMA shell and PVC is not especially perturbed by the presence of the shell. Moreover, as indicated in Table I the particles investigated in our work are almost the same size. Thus, the contribution of the second term to the partial specific adiabatic compressibility of the particles is of the same order for the different particles, and the slight increase in Figure 5 is responsible for the first term in eq. (9), that is, the

change in the adiabatic compressibility of the particle itself.

In the above discussion, a particle is regarded as homogeneous. Yao et al. proposed the model structure from an acoustic absorption study on a multilayer core/shell particle.[23] The latex consists of butyl acrylate core, PMMA shell and the intermediate phase of butyl acrylate and methyl methacrylate copolymer. The particle shell used in our work is considered to be perturbed by butyl acrylate molecules.

In order to evaluate the adiabatic compressibility of the shell part, we adopt an alternative model (model 2) that is based on the model shown in Figure 1. In model 2, the core of the particle corresponds to the C part in Figure 1; the intermediate phase between the core and PVC matrix, which is composed of the shell and the boundary layers on both sides of the shell, corresponds to
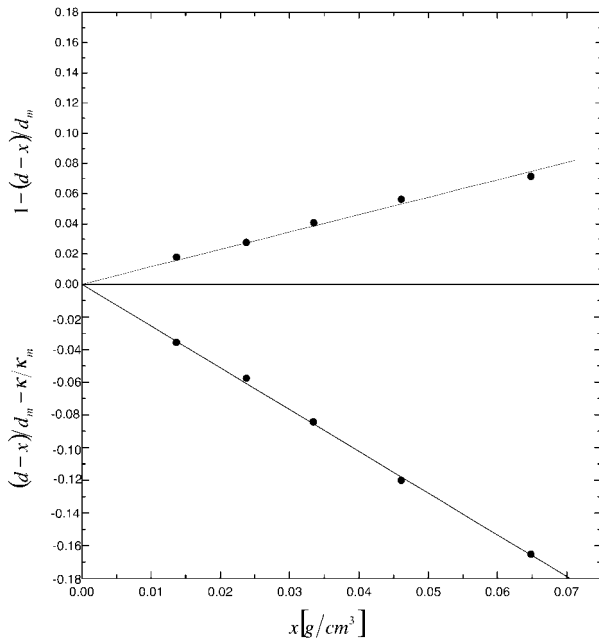
Figure 4   Plot of $[1 - (d - x)/d_m]$ and $[(d - x)/d_m - \kappa/\kappa_m]$ against concentration of particle x for sample 1.
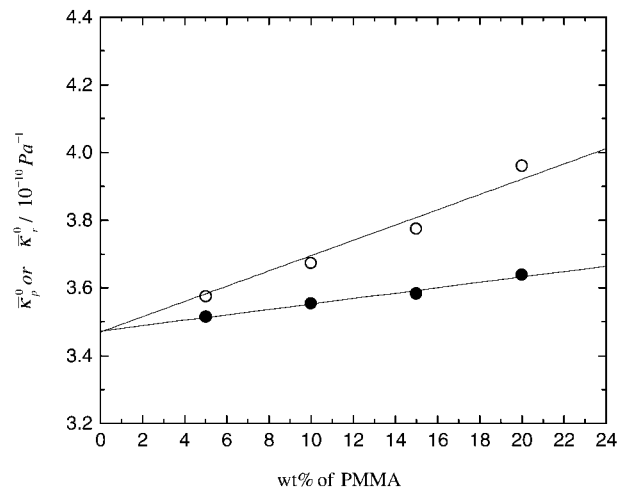
Figure 5   Plot of partial specific adiabatic compressibility against % weight of PMMA. (●) The $\bar{\kappa}_p^0$ for dispersed particles; (○) the $\bar{\kappa}_r^0$ for the particle core part. The solid lines are curves calculated by the least mean square method.

the B layer. The partial specific adiabatic compressibility of the core is thus rewritten as follows:

$$\bar{\kappa}_r^0 = \frac{v_r}{\bar{v}_r^0}\,\kappa_r + \frac{n_{MA-BA}}{\bar{v}_r^0}\,(v_{MA-BA}\kappa_{MA-BA} - v_m\kappa_m) \quad (12)$$

where the subscript MA–BA indicates the values of the shell involving the boundary layers on both sides of the shell. By analysis similar to that described in the experimental section, we can estimate the partial specific adiabatic compressibility of the rubber core. The concentration of rubber core x was calculated from the ratio of shell to core and the density data. These results are also given in Table II and are plotted in Figure 5. The partial specific adiabatic compressibility depends on the ratio of shell to core. The adiabatic compressibility of the rubber core is also obtained by extrapolating the to zero ratio of shell to core. This value is in agreement with the extrapolated value of $\bar{\kappa}_p^0$.

The change in $\bar{\kappa}_r^0$ in Figure 5 is caused by the second term in eq. (12). The unknown parameters n_{MA-BA} and $v_{MA-BA}\kappa_{MA-BA}$, which depend on the nature of the shell and the boundary layers, appear in the second term. The value of $v_{MA-BA}\kappa_{MA-BA}$ must be larger than that of $v_m\kappa_m$ ($= 1.10 \times 10^{-10}$ cm^3 g^{-1} Pa^{-1}), because of the positive slope in Figure 5. From the least linear fit of the data in Figure 5 to eq. (12) with $\kappa_r = 3.82 \times 10^{-10}$ Pa^{-1}, the slope $(v_{MA-BA}\kappa_{MA-BA} - v_m\kappa_m)/v_r$ in eq. (12) is calculated as 2.47×10^{-10} Pa^{-1}, where n_{MA-BA} is assumed to be obtained from the ratio of shell to core. The value of $v_{MA-BA}\kappa_{MA-BA}$ is estimated as 3.58×10^{-10} cm^3 g^{-1} Pa^{-1}. As the values of $v_{PMMA}\kappa_{PMMA}$ and $v_r\kappa_r$ are 1.27×10^{-10} and 3.82×10^{-10} cm^3 g^{-1} Pa^{-1}, respectively, the value of $v_{MA-BA}\kappa_{MA-BA}$ for the shell and the boundary layers is close to that of butyl rubber. The environment of the interface between PMMA and PVC may affect $v_{MA-BA}\kappa_{MA-BA}$, but as discussed previously this contribution is small. The assumption of n_{MA-BA} affects the estimation of $v_{MA-BA}\kappa_{MA-BA}$. As the value of n_{MA-BA} increases, $v_{MA-BA}\kappa_{MA-BA}$ decreases. The value of $_{MA-BA}\kappa_{MA-BA}$ changes from 2.2×10^{-10} to 3.6×10^{-10} cm^3 g^{-1} Pa^{-1} for $2R_{shell/core} > n_{MA-BA} > R_{shell/core}$, where $R_{shell/core}$ is the ratio of shell to core. A doubling of the amount of the shell, including the boundary layer between butyl rubber and PMMA, is not conceivable. The above discussion suggests that the shell, including the boundary layer between butyl rubber and PMMA, is perturbed by the butyl acrylate molecules and is so soft as to be comparable to the rubber.

In conclusion, the elasticity of the core and shell of a particle was evaluated using the two-state model shown in Figure 1 by measuring the sound velocity. The model is applicable to composite materials irrespective of the shape of additives, and can be used to obtain information about the interface or boundary layer in a solid polymer.

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