Dynamic Mechanical Properties of Polyurethane–Urea Microcapsules on Coated Paper

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SYNOPSIS

Polyurethane–urea microcapsules were prepared by an interfacial polymerization method. Dynamic mechanical measurements were carried out on the polyurethane–urea microcapsules coated on a paper substrate. The glass transition temperatures (Tg) of capsule wall were observed in the temperature scan data. Tg as the temperatures of tan δ peaks were decreased with increasing amounts of core materials. The apparent activation energies of the glass transition were estimated at about 100 kcal/mol. Master curves were obtained by shifting the tan δ spectra along the frequency axis, and the glass transition regions were unaffected by core materials studied. The shift factors were found to depend on the core/wall ratio and discussed in terms of a morphological change of microcapsules. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Microcapsules have been investigated as stimuli responsible vessels for drug delivery systems, thermal- and pressure-sensitive recording systems, etc.[1,2] In recent years, microcapsules have been successfully used for facsimile recording materials and medical image recording materials.[3,4] In these recording materials, the thermal-sensitive microcapsules are used; these are composed of the polyurethane–urea wall forming materials, the core oils with specific dye compounds, and protective colloid polymers. The color formation scheme of the materials has been proposed[3] and the release characteristics of the microcapsules have been investigated.[5] Physicochemical properties of microcapsules have been enthusiastically investigated,[1] and ultrasonic measurements were carried out for the polyurethane–urea microcapsules.[6] Dielectric measurements were carried out for microcapsule suspensions to investigate the microstructures.[7-9] The role of surfactants in polyurea microcapsules has also been reported.[10,11] However, the thermal properties of microcapsule wall membranes, which could govern the perme-

ability properties of the microcapsule, have not yet been reported.

The wall membrane is a three-dimensional cross-linked system obtained by an interfacial polymerization of multifunctional isocyanate compounds. The reaction of isocyanate groups with water molecules during this polymerization process is known to form urea crosslinks. For polyurethane networks, many articles have been published about the structure–property relationships; for instance, with dynamic mechanical analysis,[12] NMR spectroscopy,[13] dielectric dispersion analysis.[14,15] However, little is known about the polyurethane–urea network. Because the mechanical and thermal properties of the wall polymers are the fundamental characteristics controlling the permeation properties of microcapsules, we have been investigating the properties of this system. Here we report the results of dynamic mechanical thermal analysis obtained for the microcapsule-coated paper.

EXPERIMENTAL

Materials

A triisocyanate monomer (Takenate D-110N; 75% ethylacetate solution) as a wall-forming material was purchased from Takeda Chemical Co., Ltd.; this

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compound is typically obtained by an additive re-
action of trimethylolepropane (1 mol) with xyli-
lenediisocyanate (3 mol). A biuret type of hexa-
methylenediisocyanate (Sumidur N-3200) was also
used in the preparation. Tricresylphosphate (TCP:
Tokyo Kasei Co., Ltd) and cumenphenethyl (CPE:
Kureha Chemical Co., Ltd.) were used as core ma-
terials, respectively. Copoly(vinylalcohol–vinyla-
cetate) (PVA217) was used as a protective colloid.
The degree of polymerization and the degree of
acethylation were 17.00 and 15 mol %, respectively.
These materials were used for the present microen-
capsulation without further purification.

Preparation

In this article, a typical interfacial polymerization
method was employed for the microencapsulation
and described briefly. Six grams of triisocyanate
monomer solution were pored into 20 g of ethylac-
etate with a core material to obtain an organic phase.
The organic phase was pored into 3% of protective
colloid aqueous solution and immersed vigorously
using an emulsifying apparatus (Toyo Seiki Co.,
Ltd.). The resultant emulsion was stirred under the
atmospheric pressure at 40°C for 4 h. The micro-
capsules with different loading of the core materials
were prepared, and the core/wall ratios ranged from
0 to 2.0.

The microcapsule film for Fourier Transform IR
measurements was obtained, drying the suspension
on a polyethylene film, and no residual isocyanate
peak was observed in the spectra. The average di-
ameter of the microcapsule was evaluated by a light-
scattering technique using a HORIBA LA-500 an-
alyzer, and the diameters of samples were from 0.5
to 0.6 μm with almost the same distribution.

The microcapsule suspension was coated on a
plain paper substrate with a thickness of 60 μm as
a substrate using a wire bar and then kept in an
oven at 50°C to remove water. The thickness of the
microcapsule layer coated on the substrate was ap-
proximately 50 μm; it was kept in a desiccator with
a drying agent before use.

DSC measurements for microcapsules dried on a
measurement pan in a desiccator were carried out
using a Perkin–Elmer DSC-7 at a ramp rate of 10°C/
min. The film sample of aduct-type wall former
D110N was prepared by polymerizing the monomer
coated on a polyethylene film in water at 40°C for
4 h and then dried at 80°C for 1/2 h.

Dynamic mechanical measurements were carried
out using a DMTA mk-II (Polymer Laboratories
Co., Ltd.) for the microcapsule-coated paper. The
ramp rates for the temperature scan data were from
2°C/min to 5°C/min. The isothermal spectra were
obtained in the frequency range of 0.3 Hz to 10 Hz.

RESULTS AND DISCUSSION

Dynamic Mechanical Properties

Typical temperature scan spectra for the microcap-
sule without core material and the microcapsule in-
cluding TCP with the core/wall ratio of 1.0 are
shown in Figure 1 along with the results for the paper
substrate used. (The wall-forming material is
D110N.) The DSC result for the microcapsule with-
out core material showed the glass transition tem-
perature of this wall membrane at 140°C, as shown
in Figure 1. The temperature at tan δ peak for the
former microcapsule corresponds to the DSC Tg ob-
tained for the same specimen, clearly demonstrating
that the tan δ peak is due to the glass transition of
the microcapsule wall polymer. The Tg of the TCP
containing microcapsule (core/wall ratio is 1.0) is
lower than that of the microcapsule without core,
indicating a plasticizing effect of the core material,
TCP. In Figure 2, the Tg of microcapsules with dif-
ferent wall materials were plotted against the
amount of the core materials, and the plasticizing
effect of TCP seemed to be larger than that of CPE
for these microcapsules. The Tg of microcapsules
prepared from the biuret type monomer (N3200)
were found to be lower than the Tg of the aduct type
monomer (D110N), as shown in Figure 2. This could
be reasonable, since the structure of this biuret type
monomer is thought to be flexible.

The multifrequency temperature scan data were
obtained at the ramp rate of 1.5°C/min, as shown
in Figure 3. Arrhenius plots of tan δ peak positions
were obtained for various microcapsules, as shown
in Figure 4. The apparent activation energies were
calculated assuming a linear dependence in the
temperature range studied; the results are shown in
Table I. The values are approximately 100 kcal/mol
and constant for the capsules with different loading
of the core materials in TCP containing microcap-
sules (the wall former is D110N). The values are
also the same for CPE containing microcapsules.

Polyurethane elastomers prepared from multi-
functional isocyanates with diol compounds are
known to show several relaxations such as α, β, and
γ relaxation.[16] The α relaxation is related to the
amorphous glass transition, the γ relaxation is as-
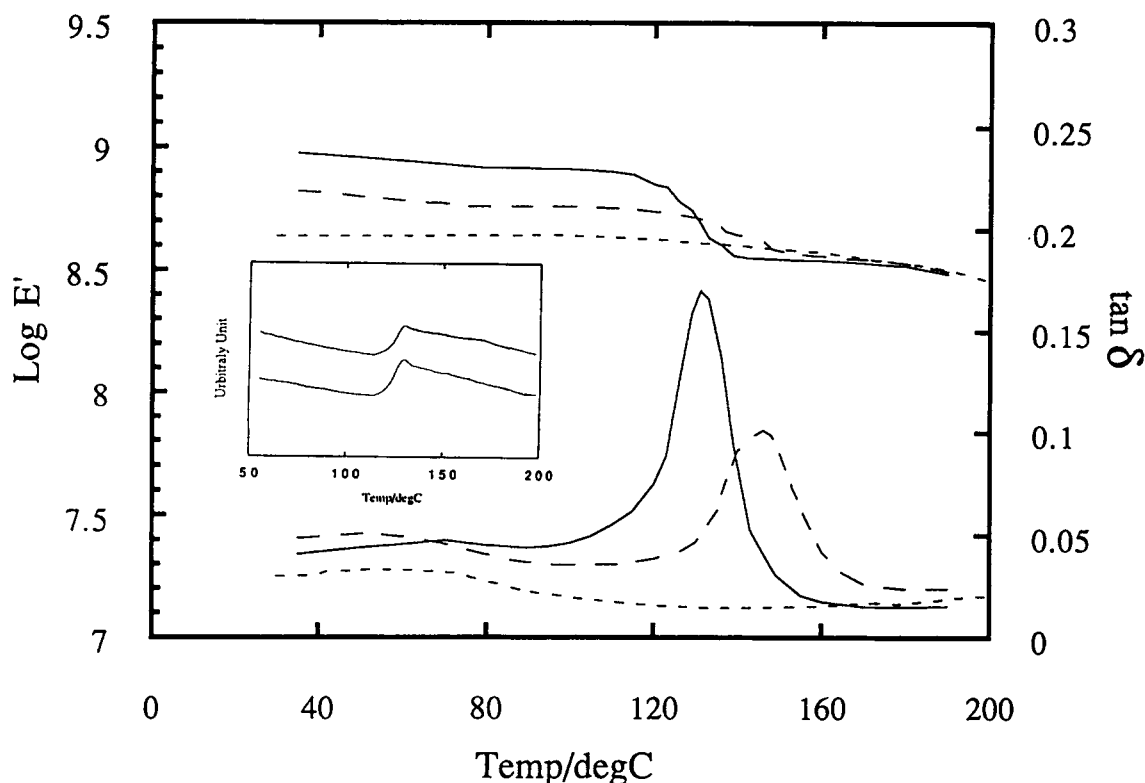sociated with motions of methylene sequences in soft

Figure 1 Dynamic mechanical spectra of microcapsules and a paper substrate used: (– –) microcapsule without core material; (———) microcapsule with TCP (core/wall ratio = 1.0); (– – – –) PVA coated paper [insert: DSC thermograms: (upper line) microcapsule without core material; (lower line) polymerized D110N film]. (D110N is used for the wall-former.)

segments, and the β relaxation is considered to be associated with motions involving water-absorbed molecules. Melting points of hard segments are also
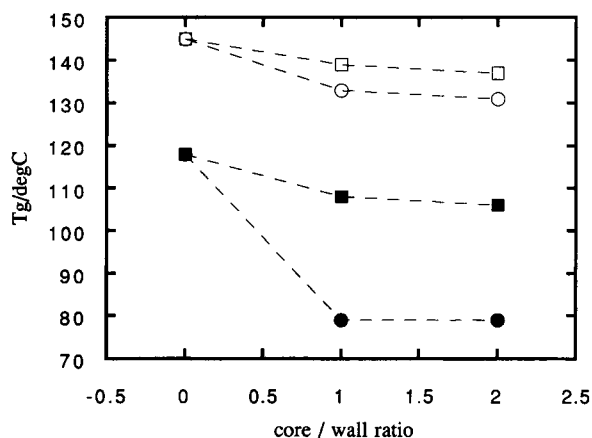
Figure 2 Dependences of microcapsule wall Tg on core/wall ratios: (○) microcapsule prepared by D110N with TCP; (□) microcapsule prepared by D110N with CPE; (●) microcapsule prepared by N3200 with TCP; (■) microcapsule prepared by N3200 with CPE.

observed in phase-separated polyurethane systems. Since the morphological structure of the present wall polymers is amorphous from a wide-angle X-ray diffraction result, the relaxation observed in the present study in microcapsules is reasonably considered to be related to the amorphous glass transition. Low glass transition temperatures on polystyrene microparticles comparing with a bulk polystyrene Tg have been observed by differential-scanning calorimetry, and it was suggested that the decrease in Tg of the particles of which diameter ranged from 20 to 60 nm was due to the high surface area to volume ratio.[17] In the present study, no significant decrease was observed, suggesting small surface effects.

The relaxation properties of polyurea systems as well as polyurethane systems are affected by intermolecular hydrogen bonding. The hydrogen bonds could give large activation energies. The introduction of core materials decreased the glass transition temperature of the microcapsule walls without affecting the apparent activation energies. The core materials TCP and CPE did not affect the hydrogen bonding structures in our microcapsules.
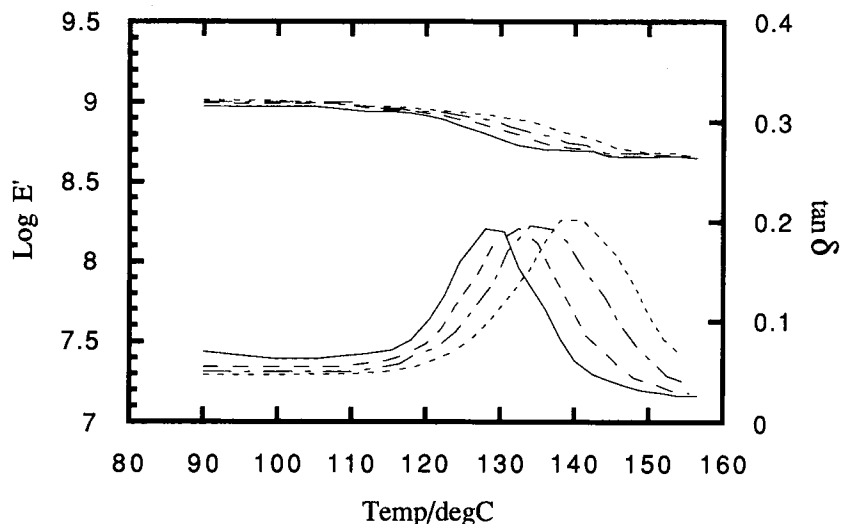
Figure 3 Typical multifrequency temperature scan spectra for the TCP including microcapsules (core/wall ratio = 1.0, D110N wall-former): (——) 0.3 Hz; (– –) 1.0 Hz; (– · –) 3.0 Hz; (– – – –) 10.0 Hz.

Williams–Landel–Ferry (WLF) Relationships

Frequency-dependences of tan δ of the microcapsule without core material at various temperatures are shown in Figure 5; the master curves obtained by shifting the tan δ plots along the horizontal axis were obtained for the microcapsules with different core/wall ratios (0, 1.0, and 2.0). The results (shown in Fig. 6) indicate that the glass transition region
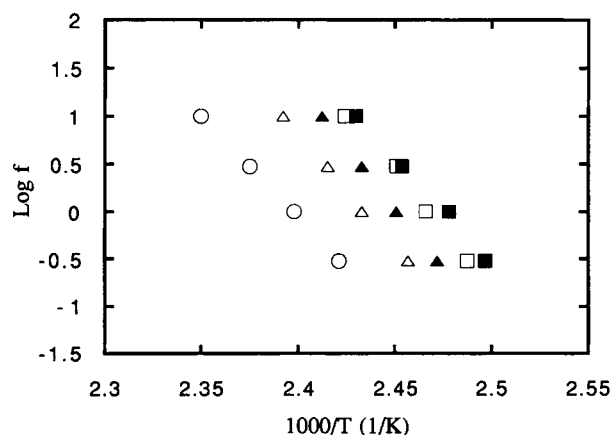
of the microcapsule wall polymer does not change when introducing the core material. The plasticizing effect of this core material TCP is the decrease of the glass transition temperature with no broadening of the relaxation time distribution. The temperature-dependences of the shift factor for these samples are shown in Figure 7, indicating a WLF-type dependence:

$$\text{Log } a_T = [-C_1(T - Tr)]/[C_2 + T - Tr] \quad (1)$$

where a_T is a shift factor and Tr is a reference temperature, and C_1 and C_2 are parameters to give the best fitted results of eq. (1) using a least-square method. The values obtained in the present analysis are plotted against the core/wall weight ratio as shown in Figure 8, and the shift factors calculated by the values are plotted in Figure 7 in the solid line, demonstrating the best fitted results.

Figure 4 Arrhenius plots for microcapsules: (○) microcapsule without core material; (□) TCP, including microcapsule (core/wall ratio = 1.0); (■) TCP, including microcapsule (core/wall ratio = 2.0); (△) CPE, including microcapsule (core/wall ratio = 0.5); (▲) CPE, including microcapsule (core/wall ratio = 2.0). (D110N is used for the wall-former.)

Table I   Apparent Activation Energies of Glass Transition Obtained for Various Microcapsules

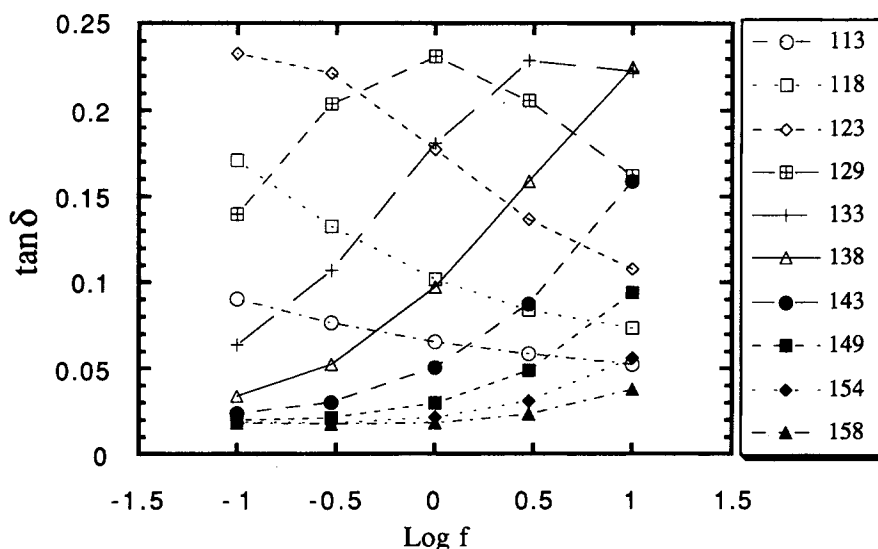| Core Material	Core/Wall Ratio	ΔEa/kcal mol^{-1}
TCP	0.0 : 1	97
TCP	1.0 : 1	102
TCP	2.0 : 1	112
CPE	1.0 : 1	109
CPE	2.0 : 1	117

Figure 5 Typical mechanical dispersion spectra at various temperatures for microcapsule without core material. (D110N is used for the wall-former.)

The C_1 and C_2 values are known to be almost constant for various polymers.[18] However, the values are also known to deviate in amorphous polymer systems, such as polymer blend systems, interpenetrating polymer network systems, plasticized systems, and so on. In the present study, the C_1 value is found to decrease when increasing the amount of core material, and to reach almost constant value as shown in Figure 8. The parameter C_1 is proportional to the inverse of free volume fraction at Tg; the dependence of C_1 on the core/wall ratio could be consistent with that of Tg as shown in Figure 2. The parameter C_2 is found to depend on the core/wall ratio in the same way as the parameter C_1. Since
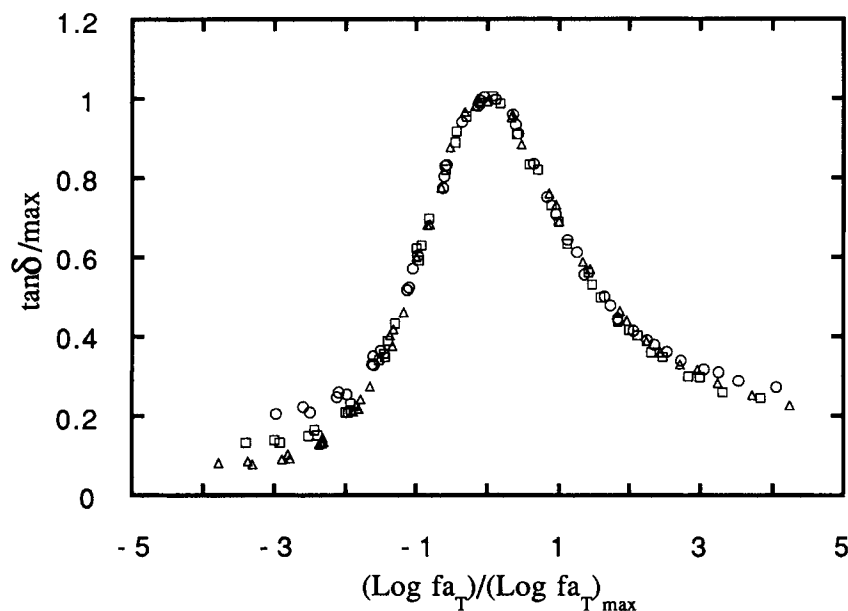

Figure 6 Normalized master curves for microcapsules with various core/wall ratios: (○) core/wall = 0; (△) core/wall = 1.0; (□) core/wall = 2.0. (TCP/D110N are used for preparation.)
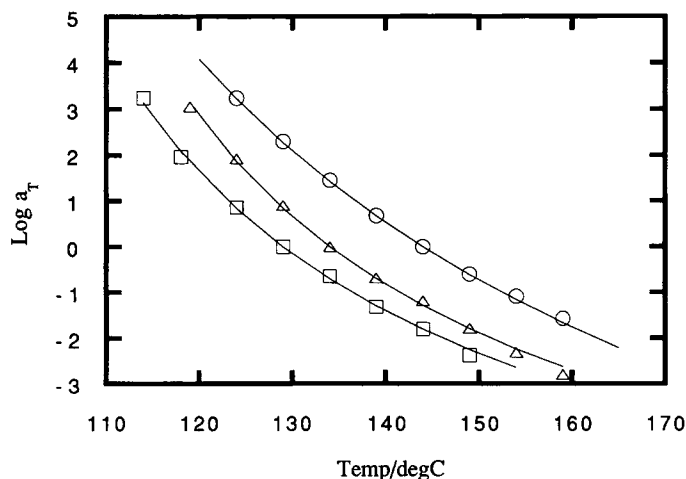
Figure 7 Temperature-dependences of the shift factor for microcapsules with different core materials: (O) TCP, core/wall = 0; (□) TCP, core/wall = 1.0; (△) CPE, core/wall = 2.0; (———) calculated. (D110N is used for the wall-former.)

the parameter C_2 is proportional to the inverse of thermal expansion coefficient, the result shown in Figure 6 indicates that the thermal expansion of the microcapsule increases when increasing the core/wall ratio. It is reasonable to assume that the core oil exists inside the wall until the amount of oil reaches a critical value, and then the oil exists outside the wall, forming the core of the microcapsule. In the present study, 0.5 to 1 of the core/wall ratio

seemed to be the critical value. Figure 9 shows the cross-sectional views of microcapsules observed by scanning electron microscopy obtained by cutting the microcapsules under liquid nitrogen temperature; a core/shell structure was found for the microcapsules of which the core/wall ratio is larger than 0.5. This morphological change could reasonably explain the dependences of C_1 and C_2 on the core/wall ratio. Little has been reported about the
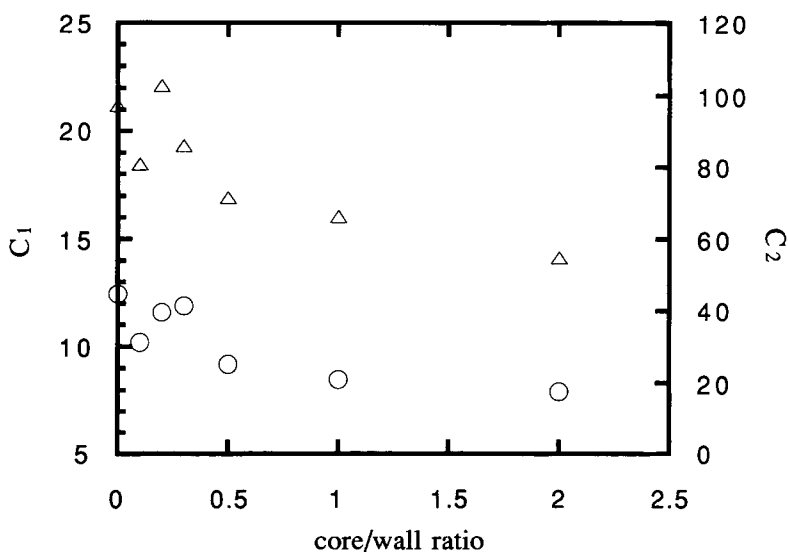

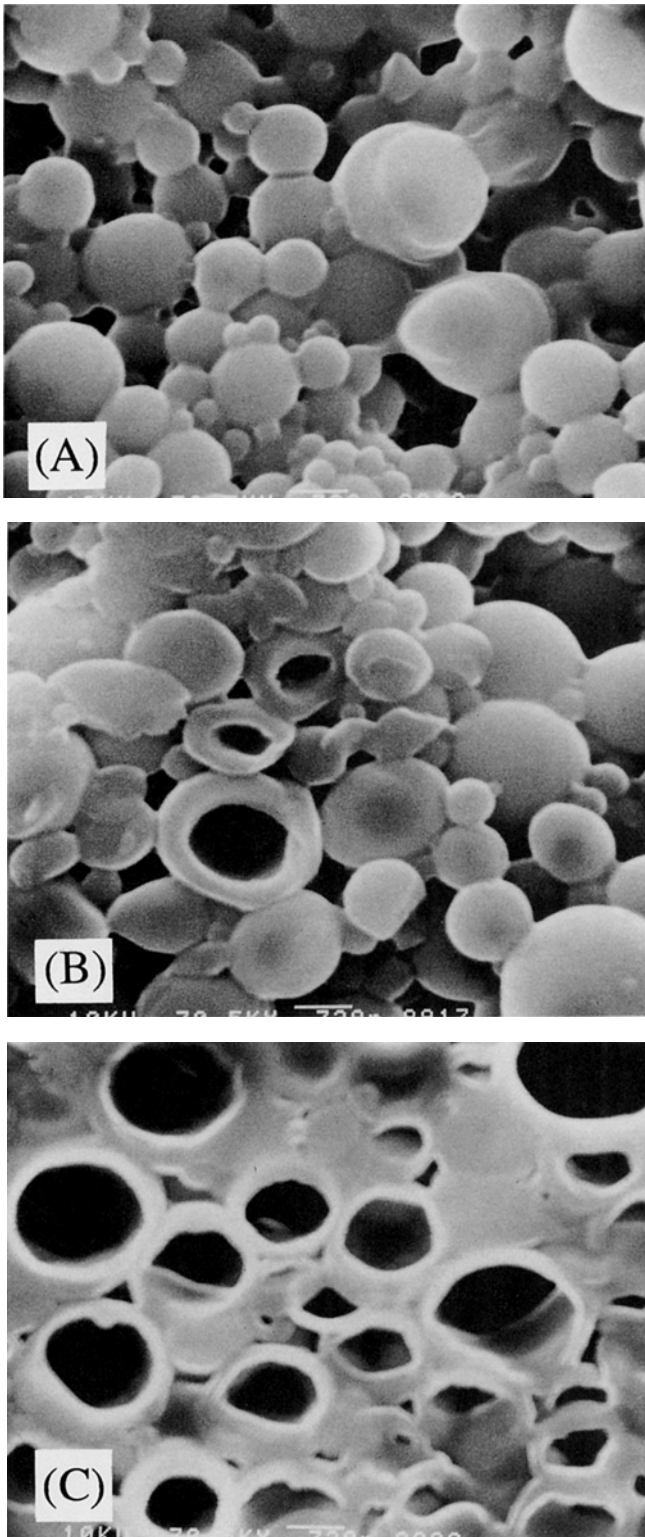**Figure 8** Dependences of WLF parameters C_1 and C_2 on core/wall ratios: (O) C_1; (△) C_2.

Figure 9 Cross-sectional views of microcapsules with different core/wall ratios of TCP obtained by scanning electron microscopy (×30,000): (A) core/wall = 0.2; (B) core/wall = 0.5; (C) core/wall = 2.0.

viscoelastic properties for polyurethane–urea microcapsule systems, and further studies are needed.

CONCLUSIONS

Dynamic mechanical properties were studied for the polyurethane–urea microcapsules, and the glass transition temperatures and WLF parameters were found to depend on the amount of the core material. The results were explained on the basis of the formation process of the core/shell structure.

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