

Emulsion rheology and properties of polymerized high internal phase emulsions

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Abstract

High internal phase emulsions are highly concentrated emulsion systems consisting of a large volume of dispersed phase above 0.74. The rheological properties of high internal phase water-in-oil emulsions were measured conducting steady shear, oscillatory shear and creep/recovery experiments. It was found that the yield stress is inversely proportional to the drop size with the exponent of values between 1 and 2. Since the oil phase contains monomeric species, microcellular foams can easily be prepared from high internal phase emulsions. In this study, the microcellular foams combining a couple of thickeners into the conventional formulation of styrene and water system were investigated to understand the effect of viscosity ratio on cell size. Cell size variation on thickener concentration could be explained by a dimensional analysis between the capillary number and the viscosity ratio. Compression properties of foam are important end use properties in many practical applications. Crush strength and Young's modulus of microcellular foams polymerized from high internal phase emulsions were measured and compared from compression tests. Of the foams tested in this study, the foam prepared from the organoclay having reactive group as an oil phase thickener showed outstanding compression properties.

Keywords : high internal phase emulsion, rheological properties, thickener, cell size, microcellular foam, compression properties

1. Introduction

High internal phase emulsions (HIPEs) are emulsions in which the dispersed phase occupies more than the maximum packing volume fraction of 0.74 for spheres all having the same diameter (Tai *et al.*, 2001). When the volume fraction of the dispersed phase is greater than the maximum packing volume fraction, the droplets are no longer spherical; they are deformed against their neighbors and take the shape of a polyhedron (Pal, 1999). Many investigators have shown the existence of a critical volume fraction beyond which the rheological properties are considerably modified. Since the rheological properties of the HIPEs are governed by a three-dimensionally interconnected network structure of thin liquid films of continuous phase, they show very complex rheological behavior. When subjected to small shear deformation, they exhibit strong storage modulus and yield stress. The deformations of the drops below the yield stress are insufficient to allow a flow in a global movement and consequently elastic behavior prevails, whereas the deformations above the yield stress are sufficient to induce a flow which is

characterized by the predominance of viscous effects. Their viscoelastic properties have been shown to depend on drop size, polydispersity, interfacial tension, volume fraction, etc (Jager-Lezer *et al.*, 1998). Among the variables, the drop size strongly influences rheological properties. A model predicting the rheological properties of HIPEs on the drop size was proposed by Princen and Kiss (1989), and several authors observed the dependence of elastic modulus on reciprocal diameter, based on this model in principle (Pal, 1999; Babak *et al.*, 2001; Pal, 2002). However, the results from Malkin *et al.* (2004) showed that the elastic modulus measured in oscillatory test and in elastic recovery as well is inversely proportional to the square of drop diameter. They explained the reasons for the discrepancy of the experimental results might be related to the type of emulsions and difference in the averaging procedure for polydisperse samples. This problem arises because the measurement of drop size is extremely difficult, especially for highly concentrated water-in-oil emulsions. Since the cell size of polymerized foam is relatively simple to be measured, it is rather easier to get a relationship between the rheological properties and the drop size of emulsion, provided that the cell size of resultant foam can directly be used as the drop size of HIPEs. Steady shear, creep recovery and oscillatory shear tests

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were carried out on a series of HIPEs.

HIPEs have a number of actual and potential applications. One of the most important applications of HIPEs is their ability to be used as open foams by the polymerization of oil phase (Barby and Haq, 1982). Open microcellular foam prepared by the high internal phase emulsion polymerization shows highly porous characteristics with regular, spherical and isotropic structure, which is quite different from the oriented, irregular structure of extruded foam that generally contains closed cell morphology with the cell size of the order of 100 microns. Due to its low density, microstructural and open cell feature, a number of applications of this foam include polymeric membranes, ion exchange resin, controlled release systems, absorbents and inertial confinement fusion targets (Bhumgara, 1995; Stokes and Evans, 1997; Duke *et al.*, 1998; Wakeman *et al.*, 1998). Two important requirements for the success in actual applications are large surface area, i.e., small cell size and good mechanical properties. Simple way to get smaller cell size is to impose higher agitation speed during the preparation of emulsion mixture. Another way to attempt is to increase the viscosity of continuous phase, which might affect the cell size and mechanical properties depending on the viscosity ratio of dispersed to continuous phases. Presumably, an introduction of thickener to the continuous phase is likely to achieve this goal. In this study, the open microcellular foams combining some thickeners into the conventional formulation of styrene and water system were prepared via highly concentrated water-in-oil emulsion followed by polymerization. Scanning electron microscopy (SEM) was used to observe the cell size as well as the microcellular morphology. Compression properties, such as crush strength and Young's modulus are important end use properties in many practical applications. Those properties of microcellular foams polymerized from high internal phase emulsions were measured from compression stress-strain tests.

2. Experimental

Styrene and divinylbenzene (DVB) were used as the monomers. Polybutadiene (PB: 420,000 g/mol of 36% cis, 55% trans and 9% vinyl; Aldrich), polystyrene (PS: 246,000 g/mol and polydispersity index of 2.14; BASF), Cloisite 10A (Southern Clay Products), and ODVC (lab-prepared) as thickeners for oil phase, Na⁺ MMT (sodium montmorillonite; Southern Clay Products) and poly(acrylamide-co-acrylic acid) copolymer (PAA: 200,000 g/mol of 80 wt% acrylamide and 20 wt% acrylic acid; Aldrich) as thickeners for aqueous phase, sorbitan monooleate (SMO) as an emulsifier and potassium persulfate (KPS) as an initiator were also used. Styrene was purified by vacuum distillation and DVB was washed with 10% NaOH solution followed by water. Syrup of 11.2 g comprised of styrene

and oil phase thickener was used as styrene solution. Other components were fixed: 150 g of water, 3.8 g of DVB, 3.43 g of SMO and 0.2 g of KPS. Code number, PB_xS_y, for example, was used to identify the PB-series, where *x* stands for PB concentration of styrene solution (thickener wt% of styrene) and *y* stands for the agitation speed in rpm. The oil phase consists of monomers, thickener and surfactant. The aqueous phase consists of distilled water, aqueous phase thickener and initiator. While the oil phase was being stirred, the aqueous phase was added dropwise. Total addition time was 30 min. Emulsion mixture was polymerized for 48 hours in a convection oven at 60°C. The polymerized mass was dried to remove the water remained in cells and residual volatiles for several days. Detailed description of HIPE and foam preparation can be found elsewhere (Williams and Wroblewski, 1988; Choi *et al.*, 2003; Lee, 2004).

The foam morphology was characterized with a scanning electron microscope (Jeol SEM 5200). The average cell size of each sample could be obtained from the image analysis technique that statistically evaluates a number of cell sizes of SEM micrographs. Rheological properties of oil phase solutions, aqueous phase solutions and emulsions thereof were measured at 25°C in a controlled stress rheometer (MCR 300; Physica) to investigate the solution viscosity of each phase, the yield stress and the storage modulus depending on thickener concentration and agitation speed. The compression tests were performed with a universal testing machine (UTM; Lloyd LR 50 K) to evaluate the compression properties of the foams. The platen speed was fixed as 0.127 cm/min throughout the tests.

3. Results and discussion

The solution viscosities of oil phase, i.e. continuous phase, and aqueous phase, i.e. dispersed phase, are shown in Fig. 1. Organoclay (C10A) viscosity shows the flow behavior of suspension and does not show zero-shear viscosity as reported by Sakai and Prestidge (2005). When HIPEs are subjected to a shear stress below a yield stress, they exhibit very small deformation indicating creep behavior. Fig. 2(a) shows the fluidity, i.e., reciprocal shear viscosity, depending on shear stress in a steady shear mode. The yield stress was determined from the onset point of abrupt increase of fluidity. Upon increasing the shear stress above the yield stress, a large increase in fluidity is observed indicating fracturing of the material. The yield stress increases with the increase of PB concentration and agitation speed. The yield stress value determined from creep-recovery response in Fig. 2(b) shows good agreement with the value from fluidity measurement in Fig. 2(a). The emulsion exhibits almost same compliance values within the stress of 2 Pa and nearly same recovery values when the stresses are removed. Thus, the yield stress of

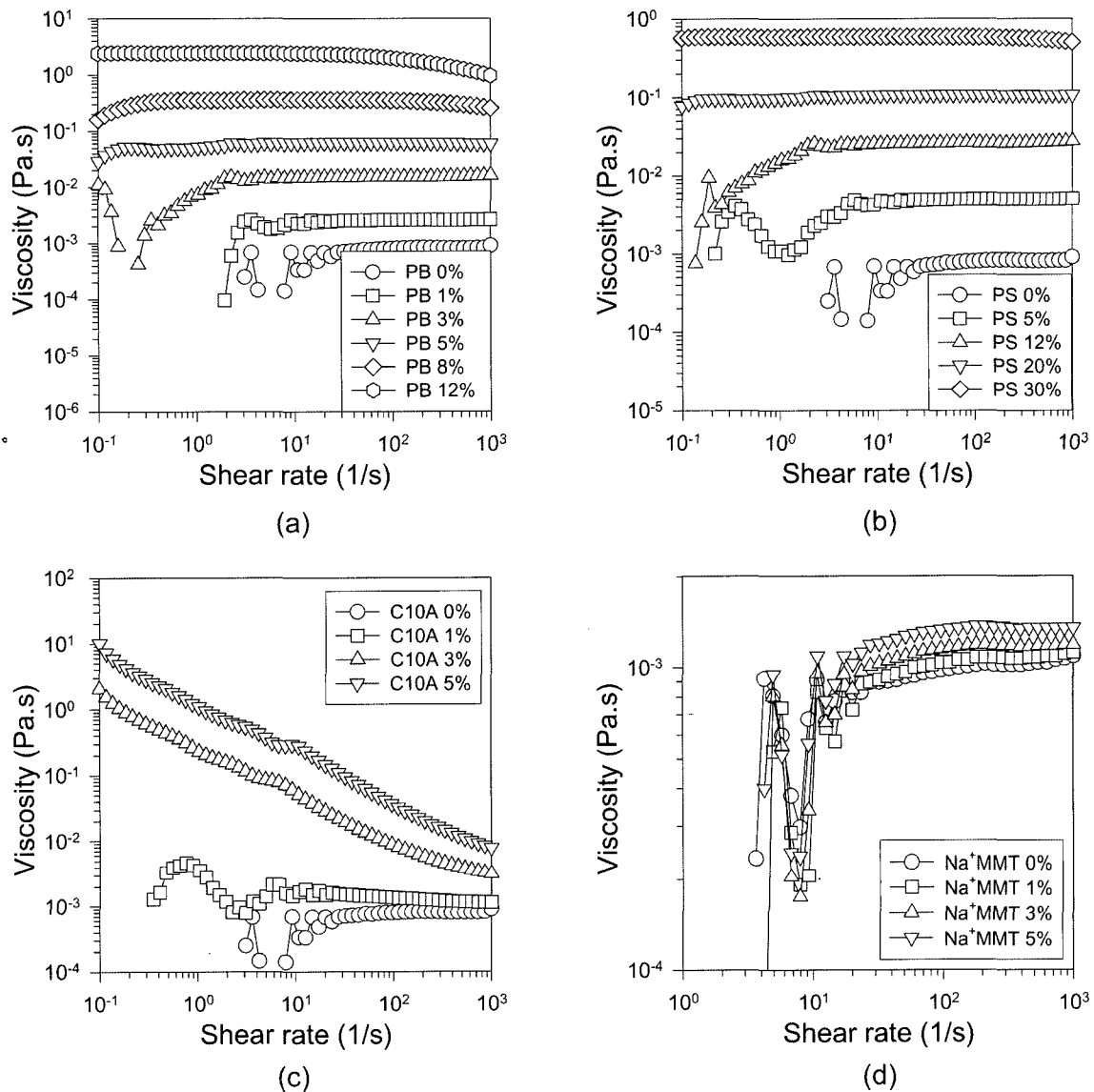


Fig. 1. Oil phase and aqueous phase viscosities of HIPES: (a) PB solution, (b) PS solution, (c) C10A solution and (d) Na⁺ MMT aqueous solution.

this emulsion is supposed to be around 3 Pa. The resultant yield stress dependence on cell size for PB3% emulsions is shown in Fig. 2(c). Princen and Kiss (1989) showed both elastic modulus and yield stress are proportional to the exponent of -1 to cell size, but a recent work by Malkin *et al.* (2004) showed elastic modulus is proportional to the exponent of -2 to the cell size. The result of our study shows the exponent of yield stress is -1.35, which is within the range of previous studies. The storage modulus data in an oscillatory shear mode are shown in Fig. 2(d) at different agitation speeds for PB3% emulsions. The storage modulus increased with an increase in the agitation speed. The reason for these increases in both yield stress and storage modulus is speculated that the radius of the dispersed phase decreased with increasing agitation speed.

The decreasing tendency of cell size when thickeners were added to the oil phase can be explained from a simplified diagram between the critical capillary number and the viscosity ratio. The critical capillary number is the critical number above which the breakup of drop takes place, and is defined as

$$Ca = \frac{\mu_c \dot{\gamma} R}{\sigma} \quad (1)$$

where μ_c is the viscosity of continuous phase and $\dot{\gamma}$ is the shear rate. The maximum stable drop size can be predicted from the relationship between the critical capillary number and the viscosity ratio. From single-drop experiments, it is known that shear flow does not lead to drop breakup above the viscosity ratio of around 4 as shown in Fig. 3 (Grace,

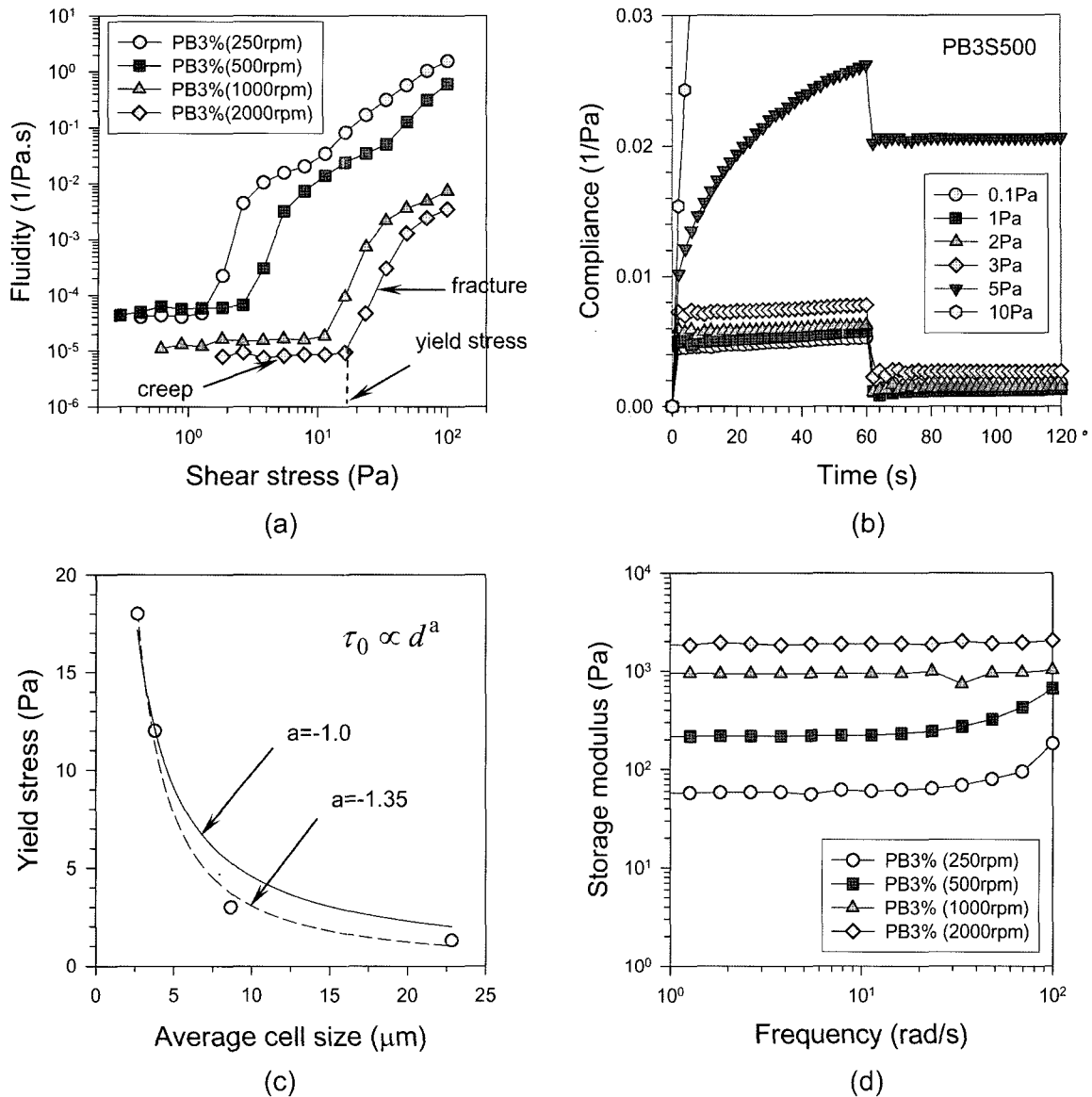


Fig. 2. (a) fluidity dependence on shear stress, (b) creep-recovery response, (c) yield stress dependence on cell size and (d) frequency at a strain of 0.5% for PB3% emulsions.

1982). In simple shear flow, the critical capillary number when the viscosity ratio is less than unity increases with the exponent of 0.6 to the viscosity ratio as the viscosity ratio decreases. As a thickener is introduced to the oil phase, the continuous phase viscosity increases and the viscosity ratio decreases. In Equation (1), drop size is inversely proportional to the viscosity of continuous phase at a given capillary number. Thus, the cell size decreases with an exponent of -0.4 as the continuous phase viscosity increases, provided that the dispersed phase viscosity is fixed. In a similar manner, it can be deduced that the average cell size is inversely proportional to the agitation speed if the viscosity ratio is kept constant. The effect of agitation speed on cell size clearly shows that the average cell size

hyperbolically decreased as the agitation speed increased, since R in Equation (1) is inversely proportional to $\dot{\gamma}$ at a given capillary number when the viscosity ratio is fixed (Fig. 9 of Lee, 2004). The results are well correlated with the theoretical predictions (Bourne, 1994). The effect of oil phase thickener concentration on cell size is shown in Fig. 3 for several PB concentrations at the specified agitation speed of 500 rpm.

The effects of oil phase viscosity on cell size for PB and PS emulsions are shown in Fig. 4. Fig. 4(a) is a replotted graph from the Fig. 3 for PB emulsions. The cell size decreases with the exponent of -0.4 to the continuous phase viscosity from the dimensional analysis as described above, and our results showed the corresponding exponent

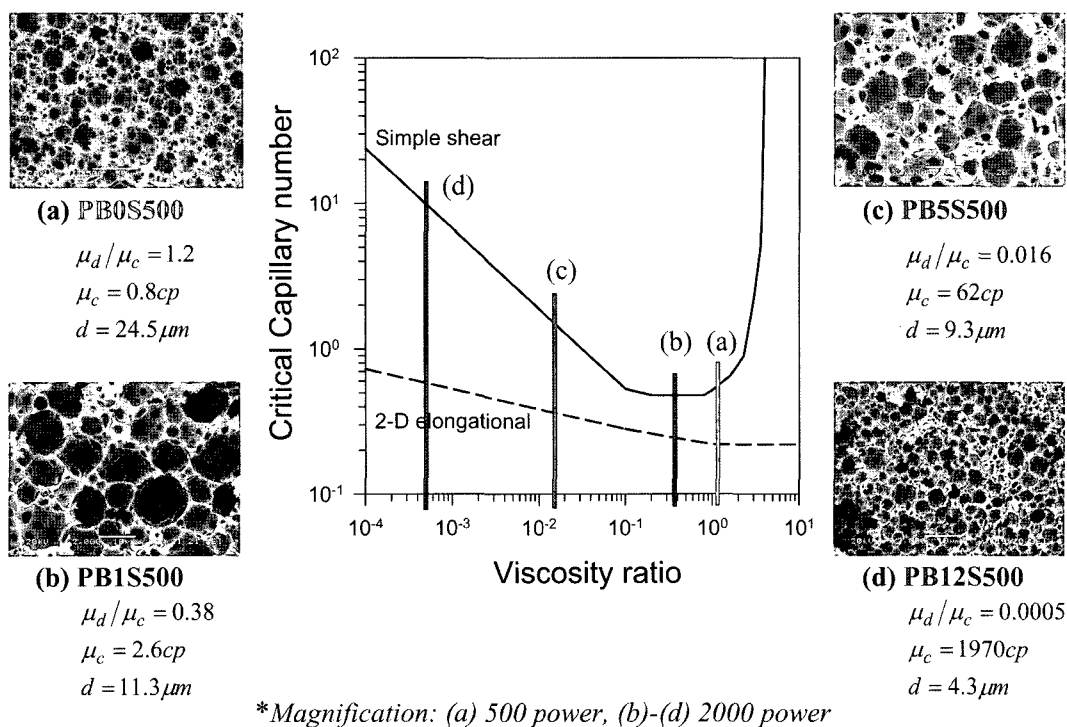


Fig. 3. Simplified critical capillary number diagram for drop breakup as a function of viscosity ratio showing the effect of thickener concentration on cell size.

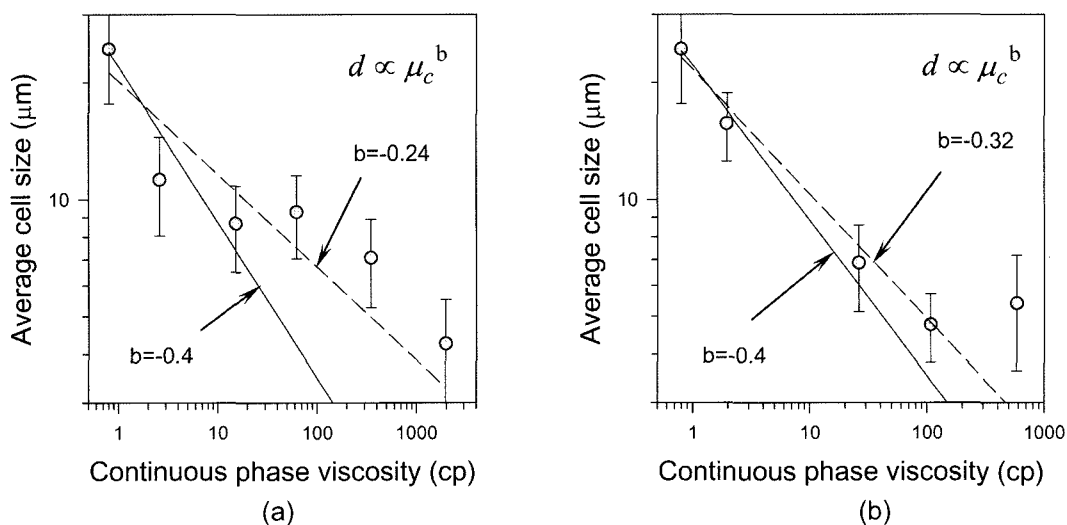


Fig. 4. Effect of continuous phase viscosity on cell size: (a) PBxS500 and (b) PSxS500.

of -0.24 for PB emulsions and -0.32 for PS emulsions. Although some mismatches are still found, it is speculated that the experimental data qualitatively follow scaling law. The effect of aqueous phase thickener concentration on cell size was also measured. With PAA as an aqueous phase thickener, the cell size increased with the addition of PAA (not shown here). The average cell size at the viscosity ratio of 4.5 and the agitation speed of 500 rpm reached

$161\mu m$. Beyond this viscosity ratio at the agitation speed of 500 rpm, stable emulsions could not be prepared.

Compression properties such as crush strength and Young's modulus of the foams were compared from compression stress-strain curves. The curves follow typical three stage foam compression behavior including a linear elastic region, a plateau region and a bulk compression region. Crush strength was calculated from the break

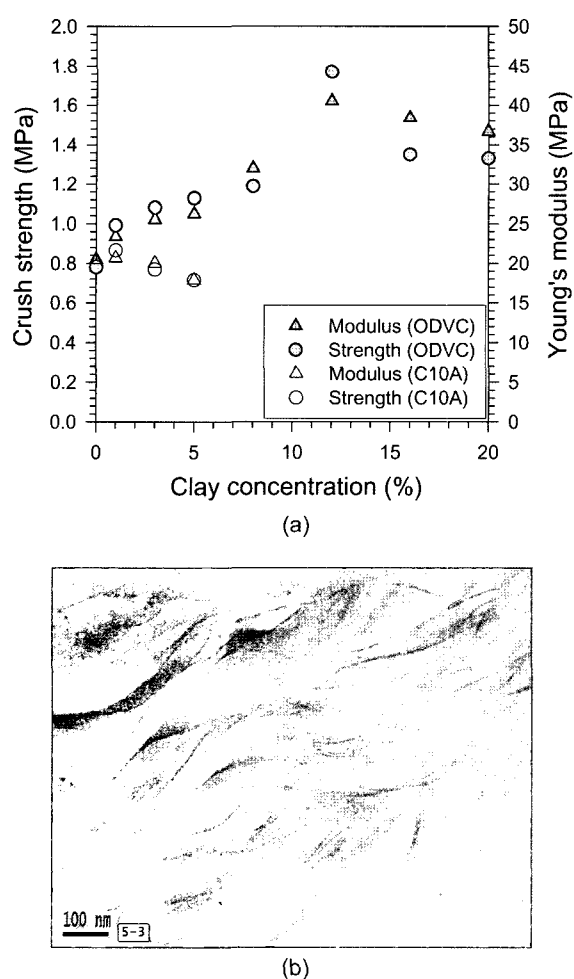


Fig. 5. (a) comparison of compression properties between the foams incorporated with ODVC and C10A as thickeners and (b) TEM micrograph showing the exfoliation of silicate layers in polystyrene matrix (*in situ* polymerized high impact polystyrene/organoclay nanocomposite composed of PB 5% and ODVC 3%).

between linear and plateau regions and Young's modulus was calculated from the slope of initial linear elastic region (Nielsen and Landel, 1994). The foams incorporated with the organoclay having vinyl group (ODVC) showed the best in compression properties among the foams investigated in this study. Compression properties of the foams incorporated with ODVC and C10A as thickeners are shown in Fig. 5(a). The foams incorporated with C10A show a little increase in compression properties up to 1% addition but monotonically decrease beyond this concentration. In the case of the foams incorporated with C10A, the silicate layers seem to be intercalated with polymerized PS chains. The TEM micrographs showing the intercalated silicate layers for the high impact polystyrene/C10A nanocomposites are found elsewhere (Kim *et al.*, 2003). However, the foams incorporated with ODVC show substantial

increase in compression properties up to 12% addition. It is suspected that the outstanding properties of ODVC foams come from a nano-structured microcellular composite. The organoclay, ODVC (octadecylvinylbenzyl clay), was prepared from an ion exchange reaction between Na^+ MMT and dimethyloctadecylvinylbenzyl ammonium bromide. Thus, ODVC participates in the polymerization of styrene. Fig. 5(b) shows a TEM micrograph of a high impact polystyrene/ODVC nanocomposite, where the exfoliated structure of silicate layers in polystyrene matrix is clearly seen. Therefore, it is concluded, from the present situation, that the achievement of exfoliated structure produces outstanding compression properties.

4. Conclusions

Rheological properties of the HIPES modified by introducing thickeners into conventional water/styrene system were investigated using a controlled stress rheometer, and then the resultant open microcellular foams were prepared using HIPE polymerization technique. The yield stress and the storage modulus were measured, the results of which showed a relationship that an increase in the yield stress is inversely proportional to the cell size with the exponent of values between 1 and 2. Compared to the conventional foams, the foams prepared with oil phase thickeners showed much finer microcellular morphology. Droplet size of the dispersed phase decreased with increasing agitation speed and continuous phase viscosity, resulting in increases of yield stress and elastic modulus. The foam incorporated with an organoclay having reactive group as thickener showed outstanding compression properties, which is speculated that the exfoliated silicate layers inside the polystyrene matrix achieve a nano-structured composite.

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