FOAMING POLYPROPYLENE-NANOCOMPOSITES

WITH SUPERCRITICAL FLUID

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Summary

Understanding the behavior of nano-sized particles or fillers in composites is of great importance in designing the porous structure of polypropylene using supercritical fluid. Along these lines, a critical overview is attempted on foaming polypropylene-nanocomposites with supercritical carbon dioxide. Under some conditions, the fine and distorted porous structure 10-1000 nm in size was found in nanocomposites, while the large and spherical porous structure several tens of μm in size was obtained in non-filled (neat) polypropylene. Such characteristic porous structure in nanocomposites is ascribed to the suppression of cellular growth by the existence of dispersed clay. This paper also discusses the correlation among the filler dispersion, foaming porous structures and the process in the liquid-liquid phase separation with supercritical fluid (SCF).

Keywords:

Supercritical carbon dioxide, Polypropylene, Porous structure, Polypropylene-nanocomposites, Dispersed clay, Liquid-liquid phase separation, Spinodal

decomposition

Introduction

The very large commercial importance of polymers has also been driving the intense investigation of polymeric composites reinforced by particles, fibers and layered inorganic fillers.[1), 2)] In particular, in the case of layered inorganic fillers, talc and mica have been traditionally attracting the most interest. However, recent advances in polymer/clay and polymer/layered-silicate nanocomposite materials[3), 4)] have inspired efforts to disperse clay-based fillers in almost any polymer available, usually in expectation of complete exfoliation of the inorganic fillers in polymer to yield the best performing systems.

On the other hand, so-called "microcellular" injection molding methods (e.g., batch, extrusion and injection), using supercritical fluids as foaming agents have been focused on recently in the field of polymer processing and molding, because this technology is one of the new important processing methods. The introduction of supercritical fluid into a polymeric material has distinguishable effects on the material's properties, for instance, effects on the part weight, heat insulation, sound-proofing and dielectric character, as well as maintaining the rate of elasticity. It also has other aspects in processing, for example, the reduction of viscosity and cycle time in molding. [5), 6)]

Although well defined studies on the technology combining polypropylene-clay nanocomposites (abbreviated as PPCN) and the microcellular foaming method have been disclosed to the public since this conference and previously by the Toyota Technological Institute, Toyota Central R&D Labs. and Kyoto University,[7)] a controlling method for the distribution of foamed cell size for PPCN has not been optimized yet. They conducted foam processing on maleic anhydride polypropylene (PPMA) without clay and with clay of a different clay content using pressurized carbon dioxide as the foaming agent in some temperature ranges and confirmed foamed PPCNs with a high cell density of 10^7-10^8 cells/cm^3 and homogeneity of cell size in a range of 20-120 μm. This is the first successful example of making a foaming porous structure of PPCN with supercritical fluid. [8)]

The intensive efforts of conducing porous structures under the supercritical atmosphere for a variety of polymers, as well as polypropylene, have been made with the homogeneity of cell size of several tens of μm. Recently, serial porous structure was successfully achieved with spinodal decomposition, and a similar kind of trial has been achieved such as that described above.[9)] This group's most recent studies on the correlation between a clay dispersion in nanocomposites and the process of phase separation under the supercritical condition have demonstrated the mechanism in which

viscosity should be controlled by clay silicates for confirming the variety of cell structures.

Experimental

The sample PPCN was prepared *via* melt extrusion mixing, using a twin-screw head at 210 , of a neat PP(*J-3000GV*, *Idemitsu* Petrochemical. Co., Ltd.), a maleic anhydride (MAH) - grafted PP and 5 wt% of dimethyldistearyl-ammonium ion-intercalated montmorillonite (organoclay, commercial name "*S-Ben NX*" supplied by *Hojun* Corporation, JAPAN). The PP modified by 2.5 wt% maleic anhydride is also a commercial product (*U-mex* 1001) from *Sanyo Kasei* Corporation, JAPAN. The MAH-modified PP (abbreviated as PPMA) has the weight-average molecular weight Mw=60000 and Mw/Mn= 4 as determined on a gel permeation chromatogragh with polystyrene elution standards in trichlorobenzene at 145 . The extruded standards were then pelletized and dried under vacuum to remove any water. Next, the dried PPCN pellets were converted into a sheet 0.3 mm thick by pressing with 5 MPa at 190   for 3 min. The melting temperature (Tm) was determined on a temperature-modulated Differential Scanning Calorimeter (DSC, *Seiko* Instruments Co., Ltd.) operated at a heating rate of 5   /min. The structure analyses were conducted using Wide-Angle X-ray Diffraction (WAXD), Small-Angle X-ray Scattering (SAXS), Transmission Electron Microscopy (TEM) and Scanning Electron Microscopy observation (SEM). Two types of batch foaming experiments utilizing the depressurization of carbon dioxide of the supercritical state were performed. One of them was conducted using a high pressure-proof cell with sapphire glass windows, which makes it possible to visualize the liquid-liquid phase separation before conducing foams by releasing high pressure. This apparatus had a CCD camera installed on the top of the lens-barrel and a video cassette recorder so that the cell formation and growth including phase separation under supercritical carbon dioxide could be recorded with a time counter (Fig. 1).   The other one was conducted using an autoclave
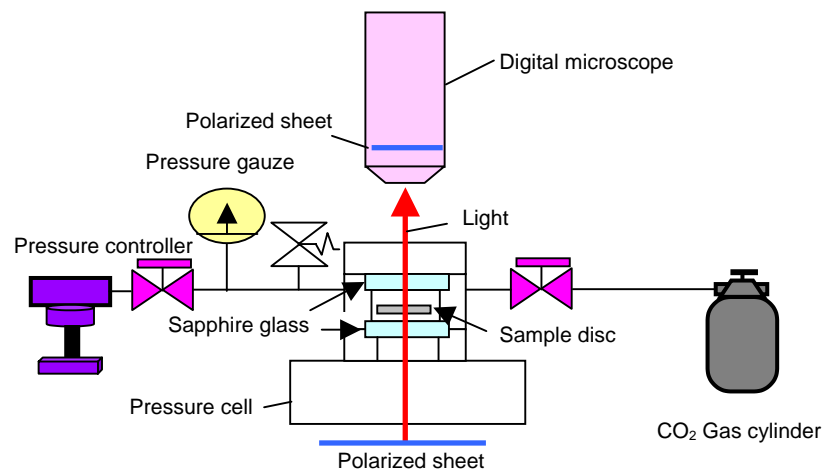
Fig. 1 Supercritical Digital Microscope system for *in-situ* observation of phase separation

Pressure gauge

Flow valve

CO₂ gas cylinder

PP-Clay nanocomposite
(PPCN disc sample)
0.3 mm thickness,
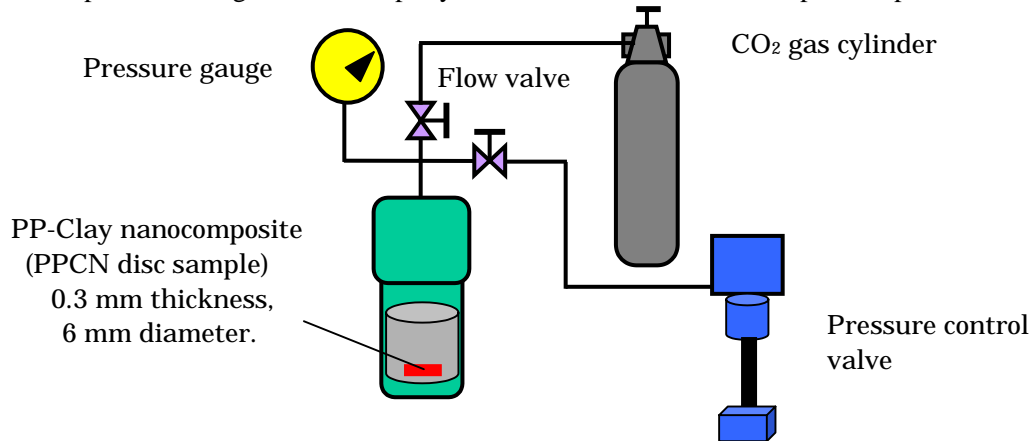6 mm diameter.

Pressure control
valve

Fig. 2 System for foaming of PP / PPCN by autoclave

(*Taiatsu Techno* Corporation, JAPAN, 300 ml), which is shown in Fig. 2.

Fig. 3 and Fig. 4 show the schematic observation process of spinodal decomposition before foaming and during foaming. The sample disc in the autoclave was heated from room temperature to 190 for 5 min to obtain a stable state of heat, and then dissolved in carbon dioxide for 60 min under high pressure (15 MPa). The gas was dissolved into the sample over a long period of time, and was completely saturated at 190 . Subsequently, once the dissolution was completed, i.e., after 60 min of dissolving gas into samples, the high pressure was quenched rapidly to super-saturate the gaseous carbon dioxide.
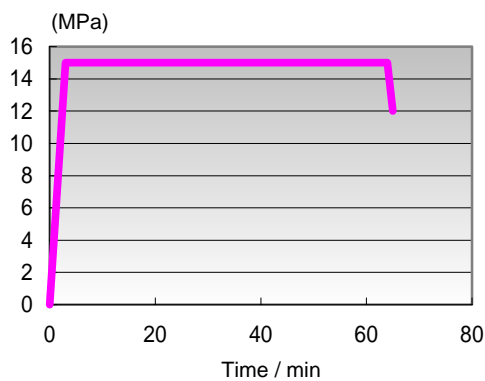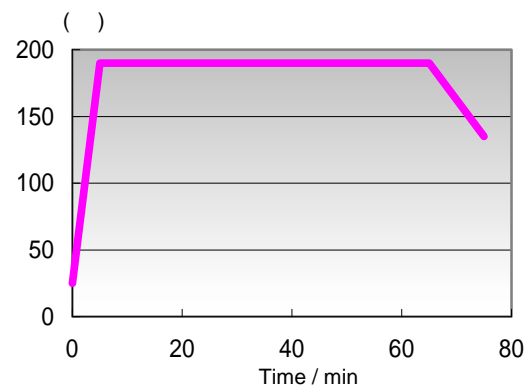
Fig. 3 Pressure profile

Fig. 4 Temperature profile

Results and discussion

a) On the observation of pre-foaming cells formation and their growth

Pre-foaming cells derived from neat PP and PPCN in a supercritical atmosphere showed great differences when observed *in-situ*.

Firstly, observation was performed with neat PP at 190 , resulting in the formation of porous structures within just a couple of minutes of starting the experiment. Then, these porous structures grew to sizes of 100-200 μm. The larger sized pre-foaming cells could be formed after an hour. This phenomena could be understood in the growth of initialized orbital cells through the liquid-liquid phase separation under the supercritical condition (Fig. 5).
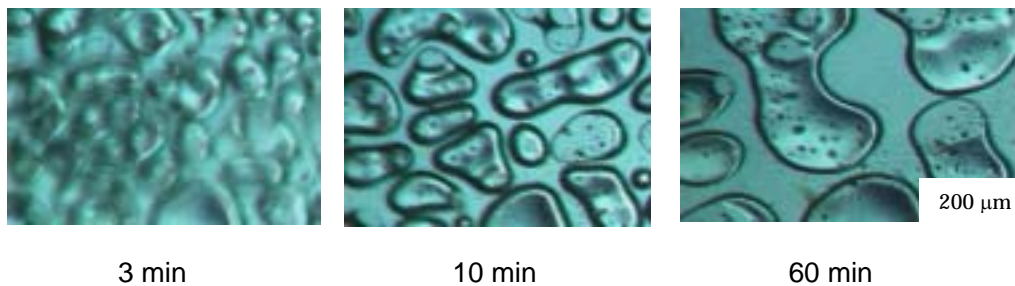

| 3 min | 10 min | 60 min |

Fig. 5　Micrographs of process for liquid-liquid phase separation (neat PP at 190)

Secondly, the same observation with PPCN instead of non-filled PP was conducted at 190 by digital microscope, resulting in great differences from those with neat PP. That is, PPCN under this condition has no obvious pre-foaming cells from molten composites even though it was observed for more than an hour (Fig. 6).
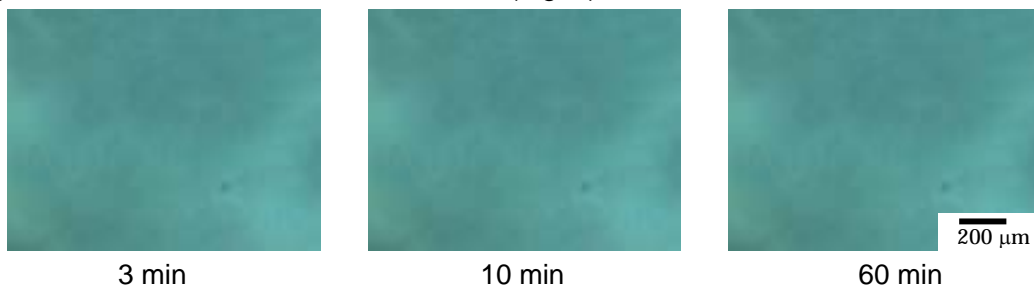

| 3 min | 10 min | 60 min |

Fig. 6　Micrographs of process for liquid-liquid phase separation (PPCN at 190)

b) <u>Tracing of the process for liquid-liquid phase separation with PPCN</u>

In order to obtain further information on phase separation under the supercritical condition, behavior among the PPCNs was compared under a different quenching temperature, 160 or 135 , respectively through *in-situ* observation without foaming or gas releasing.

One molten PPCN held for an hour at 190 under the supercritical condition dropped in temperature to 160 rapidly and was held for 1 min. It showed many

pre-foaming cells several tens of μm in size, but another PPCN treated in the same condition, and held at 135 for 1 min, resulted in no obvious pre-foaming cells over 10 μm (Fig. 7).
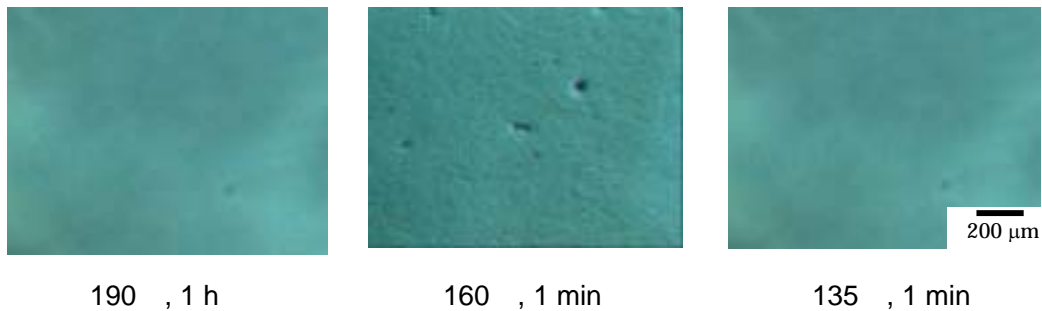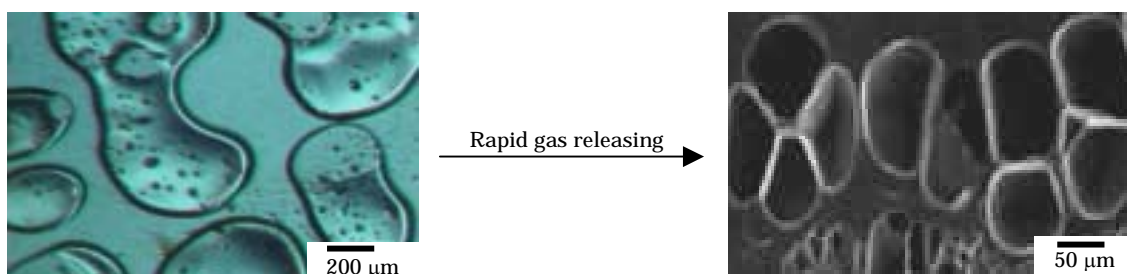

190 , 1 h   160 , 1 min   135 , 1 min

Fig. 7   Micrographs of PPCN cooled to 160, and to 135 , respectively
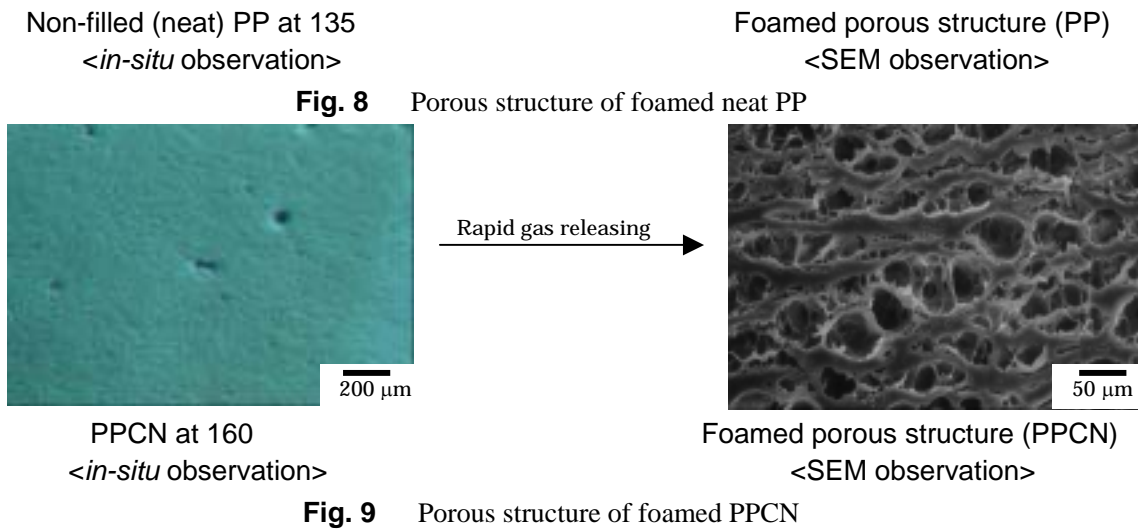
Judging from these experimental results on observation, some serial structure of porous foamed PPCNs could be imagined by simple controlling of quenching (temperature dropping) and the gas releasing conditions in an easy manner for the "architecture" in microcellular foams with nano materials.

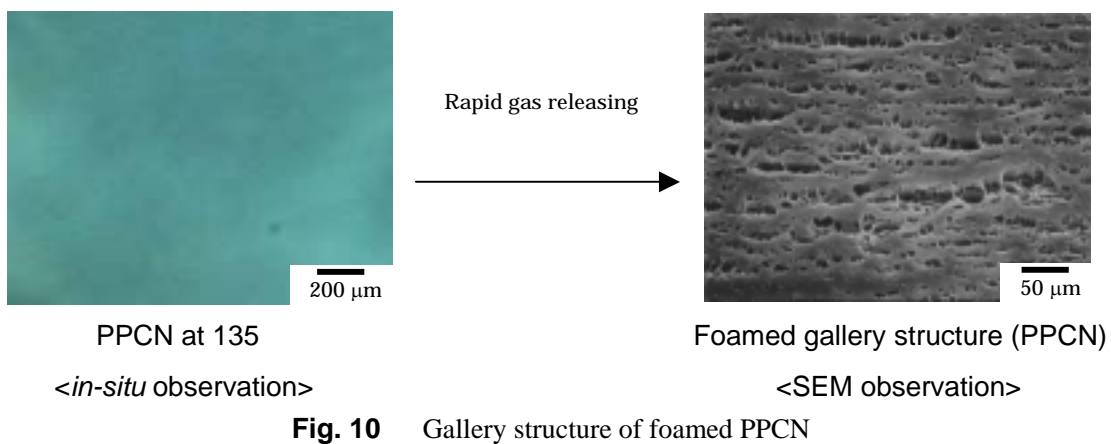c) Actual foaming of these composites and SEM observation of foam cell structure

Actually, foamed samples were made using an autoclave (Fig. 2) under the corresponding temperature schematic profile instead of the "*in-situ* observation devices" shown in Fig. 1.

The same procedure was adopted and then followed by gas releasing at a reduced temperature. Foamed disc samples were observed with SEM to investigate the cell structure concerning the correlation of pre-foamed cells and the treatment temperature. Once all samples were molten and had dissolved the carbon dioxide held for an hour under the supercritical condition (15 MPa) at 190 , they were then subjected to rapid temperature reduction to 160 or 135 , and held for 1 min, followed by gas releasing to be foamed. Fig. 8, Fig. 9 and Fig. 10 show the characteristic foam structures with a comparison of their pre-foamed phase decomposition appearances.

Rapid gas releasing

Non-filled (neat) PP at 135   Foamed porous structure (PP)
        <*in-situ* observation>   <SEM observation>

Fig. 8   Porous structure of foamed neat PP

Rapid gas releasing →

200 μm   50 μm

PPCN at 160   Foamed porous structure (PPCN)
        <*in-situ* observation>   <SEM observation>

**Fig. 9**   Porous structure of foamed PPCN

Non-filled (neat) PP was converted to a porous foam structure with very large spherical shaped cells (over 50 μm) depending on the situation of liquid-liquid phase separation under *in-situ* observation. In contrast, PPCN could shape smaller sized but more distorted porous cells (under 30 μm) than PP only, as indicated in Fig. 9. At that point, further investigation was planned in order to clarify whether the microstructure of the foamed cells under the supercritical condition could be controlled by phase degradation and its conservation.   Fig. 10 shows the results of SEM observation in the different temperature conditions: that is, the molten and saturated with carbon dioxide in the same manner, followed by treatments of cooling to 135 , holding for 1 min and rapid gas releasing. The foamed cells, the size of which is under 50 μm, are gallery-shaped in appearance and located in random directions.

Rapid gas releasing →

200 μm   50 μm

PPCN at 135   Foamed gallery structure (PPCN)

<*in-situ* observation>   <SEM observation>

Fig. 10   Gallery structure of foamed PPCN

d) On the correlation between porous structure and clay particle dispersive situation

Judging from the result of SEM for foamed cell structure, discussion is required on the phase decomposition under the supercritical condition, clay particle dispersion and the foaming mechanism. A serious TEM observation of foamed cells and their surroundings with PP or PPCN comparison gave much pause for thought and enlightenment when the foams made their appearance. Foamed cells at 135 , were a suitable choice of sample for

5 μm
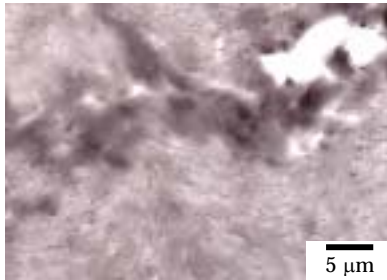
this discussion because of their characteristic cell shape and their arrangement in the cell structure. Interestingly, clay particles were dispersed in shaped cells nearby at random. A corresponding schematic drawing of the right side of a real TEM picture is shown in Fig. 11.

Foamed cell and clay dispersion
(PPCN at 135)

Fig. 11 TEM observation of foamed cell and c

In this drawing, the randomness of the dispersed clay   n the movement or rearrangement *via* the liquid-liquid phas   itical condition. A precise observation in a TEM photomicrograph of holes after foaming has proven that a lot of fine and tiny holes are located around one cell and dispersed nano clay particles can be detected with different "clay density." This means that nano clay particles near the hole set their spaces close together, while the other part without holes sets the clay particles apart. This can also be understood by comparing the two TEM photographs indicated in Fig. 12.   The existence of nano-sized clay particles and their existing density in

100 nm

Before treatment with SCF

After treatment with SCF, and foamed
(Temp. dropped 190 to 135)

Fig. 12   TEM observation and comparison of dispersed clay particle

the PP matrix can affect on the foamed cell size and microstructure.

In PPCNs, clay particles are dispersed homogeneously and through the following melting, saturation with carbon dioxide and liquid-liquid phase separation under the supercritical condition, nano particles performed an "anchor" effect on the resin matrix base and controlled the size of the cells, as shown in Fig. 13. In other words, the non-anchored part without clay particles could produce foams selectively.
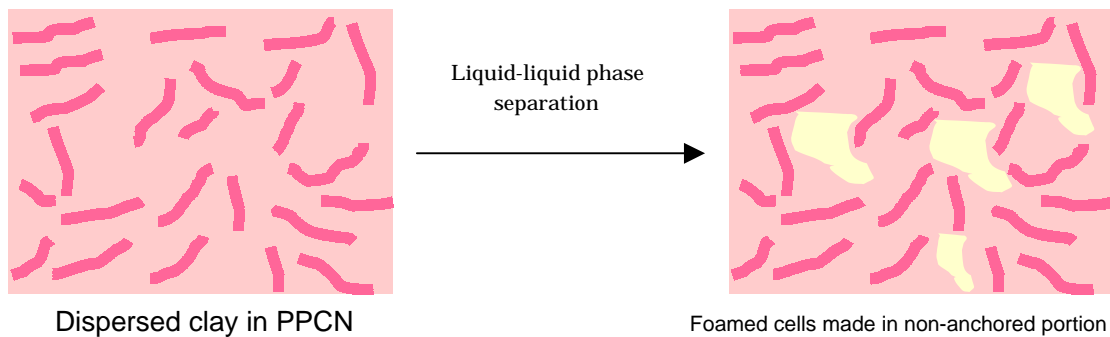
Liquid-liquid phase separation

Dispersed clay in PPCN

Foamed cells made in non-anchored portion

Fig. 13   Schematic mechanism of shaping foams in PPCN

Conclusions

For the regulation of the "microcellular" molding method example in the autoclave, nano-composite particle formation can be achieved by controlling of the liquid-liquid phase separation under supercritical fluid in some moderate temperature conditions. An attempt to clarify the mechanism of pre-foamed cellular growth with an *in-situ* microscope and TEM/SEM observation in foamed nanocomposite does explain that the fine and distorted porous structure 10-1000 nm in size is ascribed to the suppression of the cellular growth by the existence of the dispersed clay, the so-called "anchor" effect.

This is the first experimental investigation into the process of pre-foaming cell formation including liquid-liquid phase separation, though there have been many research precedents *via* the *in-situ* foaming observation.

Due to this research, the regularity of cell size and its structure can be understood from the perspective of nano particle dispersion and pre-foaming cell size controlled by temperature.

As further research, the method for confirming dispersion and interaction between the particle and matrix resin should be discussed. Additionally, it will be necessary to establish the methodology controlling the conditions in a real metallic mold.

References

1) S. Al-Malaika, A.Golovoy and C.A. Wilkie, editors.
   Chemistry and Technology of Polymer Additives. Blackwell Sci., Oxford, 1999.
2) D. Solomon and D. Hawthorne.
   Chemistry of Pigments & Fillers. Krieger, Malabar, 1991.
3) E.P. Giannelis, R.Krishnamoorti and E. Manias,
   Advances in Polymer Science, **138**: 107, 1998.
4) M. Alexandre and P.Dubois,
   Mat. Sci. & Eng. R: Reports, **28**: 1, 2000
5) J.S. Colton and N.P. Suh,
   The Nucleation of Microcellular Thermoplastic Foam: Process Model and Experimental Results. *Advanced Manufacturing Process*, 1986. 1 (3&4): 341-364.
6) Collias, D.I., D.G.Baird and R.J.M.Borggreve,
   Impact Toughening of Polycarbonate by Microcellular Foaming. *Polymer*, 1994, **35** (18): 3978-3983.
7) P.H. Nam, P. Maiti, M. Okamoto, T. Kotaka, T. Nakayama, M. Takada, M. Ohshima and A. Usuki, Foam Processing and Cellular Structure of PP/Clay Nanocomposites, *Nanocomposites 2001 proceedings*, **2001**, ECM.
8) M. Okamoto, P.H. Nam, P. Maiti, T. Kotaka, T. Nakayama, M. Takada, M. Ohshima, A. Usuki and H. Okamoto. *Nano Lett.*, 1(9), 503-505.
9) D. Narushima and H. Saito. *Japan Soc. Poly. Pro. '01 Tech. Papers*, 157 (2001).

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