EFFECT OF FLUORINATED HYPERBRANCHED POLYMER ON FOAMING OF PMMA

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Abstract

The effect of fluorinated hyperbranched polymer on the foaming of PMMA using supercritical carbon dioxide (scCO2) was investigated. In order to enhance cell nucleation we used the fluorinated hyperbranched polymer. The foaming behavior was determined in dependence upon an amount of the fluorinated polymer. The introduction of the fluorinated polymer remarkably reduced the size of foaming cells of PMMA. Furthermore, the cell number density was significantly changed by a presence of the fluorinated polymer. This finding can be explained by the enhanced nucleation generated from the well-dispersed fluorinated hyperbranched polymer as nucleating agent.

Introduction

Polymeric foams are used in many applications because of thermal conductivity, light weight, low dielectric constant, sound damping and optical properties [1, 2]. Supercritical carbon dioxide ($scCO_2$) is used as environmentally benign physical blowing agent. CO_2 has many advantage such as non-toxicity, non-flammability, low cost and chemical inertness. $scCO_2$ has high solubility, low interfacial tension and excellent surface wettability. It has been reported that the use of $scCO_2$ as a physical blowing agent enables creation of well-distributed micron size closed cellular structure that is beneficial in mechanical strength compared with heterogeneous or open cell structure.

The final properties of the polymeric foams depend on the cellular diameter, diameter distribution, porosity and cell number density. Inorganic fillers are used to control the cell size and the distribution. According to the concept of cellular nucleation, during nucleation process gas molecules overcome an energy barrier to form stable nuclei. In order to generate fine pores with small diameter distribution, nucleation at the same time is required following rapid depressurization. In this sense, the utilization of fillers is beneficial. Fillers reduce activation barrier of free energy for nucleation and enhance inhomogeneous nucleations at interface between fillers and matrix polymer. The dissolved gas is distributed into the fillers, leading to the small cells and high cell number density with narrow size distribution. The cell size and density depends on the filler size, the size distribution and surface chemistry. Chiu et al. [3] reported that addition of calcium carbonate led to the reduced cell size and increased foam number density of polystyrene. Chang et al. [4] reported the effect of nanoclays on the cellular structure of polyethylene-octane copolymer. Their results indicated the lowered average cell size and increased cell density. In a different study, Goren et al. [5] studied the effect of surface chemistry on the cellular structure of PMMA. They showed that surface treatment by fluorination led to decrease of the cell size due to the reduced free energy barrier for nucleation.

There are only few studies reporting that use of fluorinated polymer for polymeric foams. Yokoyama et al. [6] reported the foaming of polystyrene-*block*-poly(perfluorooctylethyl methacrylate) diblock copolymer. Their results suggest that nanocellular structure was generated in the phase separated spherical domains which had high solubility in CO_2. In this case the temperature of foaming is crucial. CO_2 soluble domains form cellular structure, while the another glassy block phase suppresses the cell growth. The temperature should be between glass temperatures of two block phases in order to prevent over-expanding.

In the current study, we focused on the use of hyperbranched polymer in which the end groups are fluorinated. The effect of the fluorinated hyperbranch polymer on the foaming behavior of poly(methyl methacrylate) (PMMA) was studied by using scCO2 in terms of the fluorinated polymer concentration and foaming temperature. It is expected that the fluorinated polymer has high dispersion due to the compact dendritic architecture and the effect as nucleation agent due to end group fluorination. The cellular structure such as size, size distribution and number of cell density was remarkably changed due to a presence of the hyperbranch polymer.

Materials and Methods

A commercial PMMA (“PARAPET G”, Kuraray Co., Ltd.) was used. The melt flow rate at 230^{o}C is 8.0 g/10min and the density is 1.13 g/cm^3 at room temperature. We used fluorinated hyperbranched polymer HBP-1 which has compact spherical molecular size and high compatibility to PMMA as an additive to PMMA. The weight-average molecular weight is

16,000 g/mol (conventional GPC column calibration by using polystyrene standard) and the glass transition temperature is 81°C. PMMA and HBP-1 was blended as weight ratio of 0.01, 0.03, 0.1, 0.3, 1 and 3 wt% by internal mixer (Labo Plastmill, Toyo Seiki Seisaku-sho, Ltd.) at 190°C for 5 min. The blended samples were press molded into sheets of thickness of 1~2 mm at 190°C.

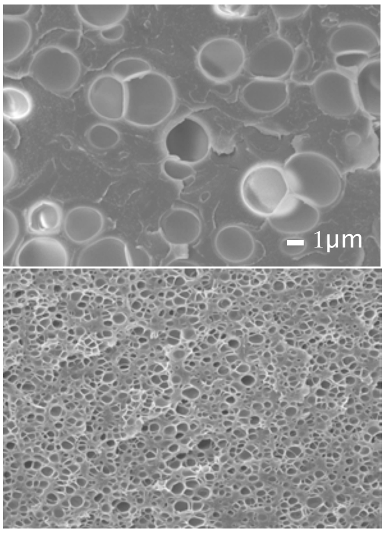
The film samples prepared in the described above were inserted into autoclave (Taiatsu Technology Co.). The whole setup was heated to the final temperature of 40~100°C by a heating jacket. After reaching the constant temperature CO_2 was loaded up to the foaming pressure of 15 MPa until saturation of CO_2 in the sample films. The foaming was carried out by a rapid release of the pressure of CO_2 by the supersaturation of the polymer films with CO_2. The saturation time was 8 hr. We confirmed that the time was sufficient to absorb CO_2 until saturation state by the gravimetric method. The depressurization from 15 MPa to ambient was completed in about 2 s.

The density of the foamed film was determined from the sample with diameter of 20 mm by the means of buoyancy method. The porosity V was calculated from the unfoamed and foamed density, ρ_0 and ρ_f, respectively:

$$V = 1 - \frac{\rho_f}{\rho_0} \qquad (1)$$

The morphology of cell structure was visualized by field emission scanning electron microscopy (FE-SEM, JEM-7600F, JEOL Ltd.). The average cell diameter D and the distribution were determined by using the image analysis software (Mac-view, Mountec Co., Ltd.) from 1000~3000 cells. The cell number density N_f was obtained by the density of unformed and foamed samples and average cell diameter:

$$N_f = \frac{6(\rho_f/\rho_0 - 1)}{\pi d^3} \qquad (2)$$


(a)

(b)

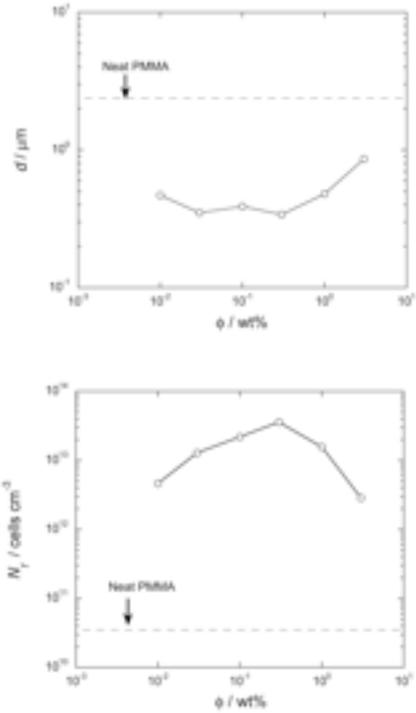
Figure 1. Scanning electron micrographs of the cross sections of (a)PMMA and (b) PMMA blended with fluorinated hyperbranched polymer of 0.3 wt% foamed at 50°C.

Results and Discussion

Effect of Additive Amount on the Foaming

Figure 1 shows SEM image of cross section of PMMA/HBP-1 films foamed at 50°C. Here the neat PMMA and PMMA contained HBP-1 of 0.3 wt% are just shown. Surprisingly, an introduction of a small amount of fluorinated dendritic polymer caused remarkable reduction of cell diameter as shown in Figure 1. Furthermore, an apparently increased number of cell can be observed in comparison with neat PMMA.

The quantitative analysis of the foaming morphology is plotted in Figure 2 (a and b) for the cellular structure of PMMA incorporated with HBP-1 of 0, 0.01, 0.03, 0.1, 0.3, 1.0 and 3.0 wt%. It is clear that a very small amount of HBP-1 even at 0.01 wt% has a


(a)

(b)

Figure 2. Effect of fluorinated hyperbranch polymer content on (a) average cell diameter and (b) cell density foamed for PMMA/HBP-1 foamed at 50°C.

beneficial impact on the foamed cell structure. The decrease of cell diameter was found for whole range of content of the fluorinated hyperbranch polymer (HBP-1), starting with 2.4 μm for neat PMMA to 0.34 μm at 0.3 wt%. With increasing the content of HBP-1, number of the large cell with a diameter of about 1 μm slightly decreased and distribution of the cell size became narrow, while the average diameter was not that different within 0.3 wt%. Above 0.3 wt%, the diameter showed a tendency to increase. On the other hand, the number density of cell N_f showed jump from 3.8×10^{10} to 4.6×10^{12} by an addition of the HBP-1 of 0.01 wt% as shown in Figure 2b. N_f reached a peak value 3.6×10^{13} at 0.3 wt% of HBP-1. Above 0.3 wt%, N_f decreased as increasing the content. Although we will discuss the increased diameter and the decreased cell number density above a critical concentration as increasing HBP-1, this is open question at present.

Figure 3 shows cell size distribution of PMMA and PMMA incorporated with HBP-1 of 0.01, 0.03 and 0.3 wt%. Note that x-axis of this column plot is not equally spaced intervals due to a limitation of the analysis software. For example, the values of x-axis at 0.1 and 1 μm represents the frequency of cells with $0.1 \leq d < 0.2$ and $1.0 \leq d < 2.0$ μm, respectively. As shown in the figure neat PMMA shows broad cell diameter distribution. When adding HBP-1 of 0.01 wt%, the diameter distribution suddenly shifted towards small size. This means that HBP-1 well dispersed into PMMA and played an important role as nucleating agent, in spite of very small amount of additive amount. Here we should note that the distribution had a bimodal shape with long tail, while main peak was present in the low diameter. With increasing HBP-1, the tail disappeared and the distribution converged into single distribution, resulting in Gaussian-type distribution. There was little change in the peak of the frequency in spite of the content. We consider that the dispersed fluorinated hyperbranched polymer affected the number of nucleation sites, but 0.01 wt% was insufficient to cover whole the volume and to generate heterogeneous nucleation throughout the sample.

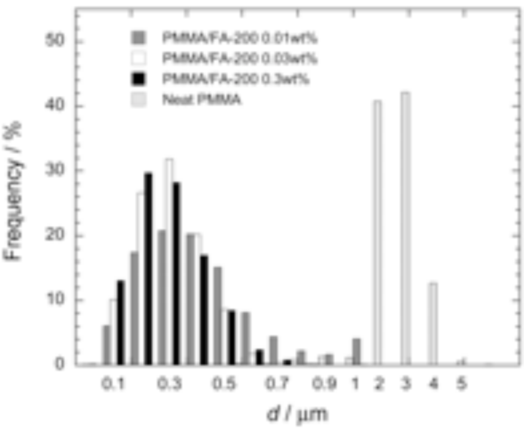


Figure 3. Effect of fluorinated hyperbranch polymer content on (a) cell diameter and (b) cell density foamed for PMMA/HBP-1 foamed at 50^{o}C.

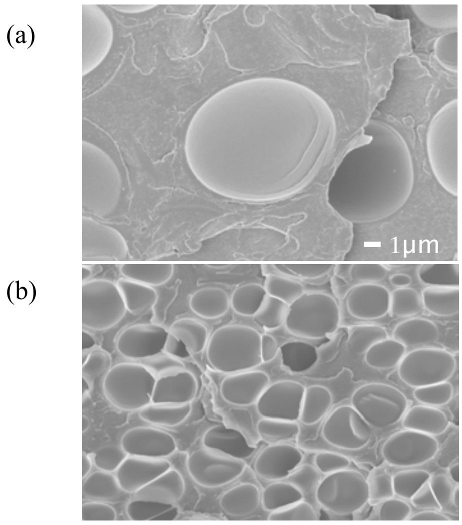


Figure 4. Scanning electron micrographs of the cross sections of (a)PMMA and (b) PMMA blended with fluorinated hyperbranched polymer of 0.3 wt% foamed at 80^{o}C.

Effect of Temperature on the Foaming

One of the dominant parameters to control the cellular structure and void fraction is the foaming temperature. It strongly affects not only the viscoelastic behavior of the polymer but also the solubility and diffusion coefficient of the gas. The solubility of the gas generally decreases with the elevated temperature due to negative value of solution enthalpy of the gas into polymer. Therefore, the reduced gas dissolved in polymer gives rise to a small amount of nucleation sites. Furthermore, the increased temperature enhances the diffusion coefficient of the gas, resulting in small number of nuclei. The higher temperature brings less elastic behavior and low viscosity of polymer. This leads to the large deformation of the softened cell membrane under the low stress. Figure 4 shows the SEM micrographs of PMMA and PMMA containing HBP-1 of 0.3 wt% foamed at 80^{o}C. Comparing with Figure 1, the cell diameter of PMMA became large and the cell number decreased apparently. For PMMA/ HBP-1 blend, the cell structure was larger and number of cell was smaller than those of the foams obtained at 50^{o}C. However, it is clear that the fluorinated hyperbranch polymer still influenced the cellular structure at the temperature, though the difference between neat PMMA and PMMA/HBP-1 seems to be small comparing with that at 50°C.

Effect of Viscoelastic Behavior on Foaming of PMMA/HBP-1

As shown in Figures 1-4, the fluorinated hyperbranch polymer has remarkable effect on the foaming behavior of PMMA. Here we will discuss the effect of the additive on the viscoelastic behavior of PMMA. The foaming was carried out at 40~100°C. This is below or close to the glass transition temperature (T_g) of PMMA. However, the adsorption of gas provide the plasticization of polymer. It enhances the mobility of polymer chain: depression of T_g and the melting temperature. Therefore, we examined the rheological measurements of PMMA melts above $T_{g.}$ The dynamic viscoelastic measurements were carried out at 150~230°C. The time-temperature superposition was valid for all the samples including PMMA/HBP-1 blends. Figure 5 indicates mastercurves of storage modulus (*G'*) and loss modulus (*G"*) of PMMA and PMMA blended with fluorinated hyperbranched polymer at a reference temperature of 190°C. Neat PMMA showed typical viscoelastic behavior of flexible polymer with moderate molecular weight distribution. At high frequencies the clear plateau modulus which can be relevant with the entanglement of polymer chains was invisible. The terminal flow behavior was seen at low frequencies: $G' \propto \omega^2$, $G'' \propto \omega^1$. All the curves of PMMA/HBP-1 were superimposed on that of the neat PMMA irrespective of the content. In Figure 2, high concentration of HBP-1 above 0.3 wt% gave rise to increase of cell diameter. The molecular weight of HBP-1 is much lower than that of PMMA used here. However, it is not the case. The variation of the rheological behavior over the wide range of frequencies with addition of HBP-1 was not confirmed, so that we can say that the foaming behavior cannot correlate with the rheological change.

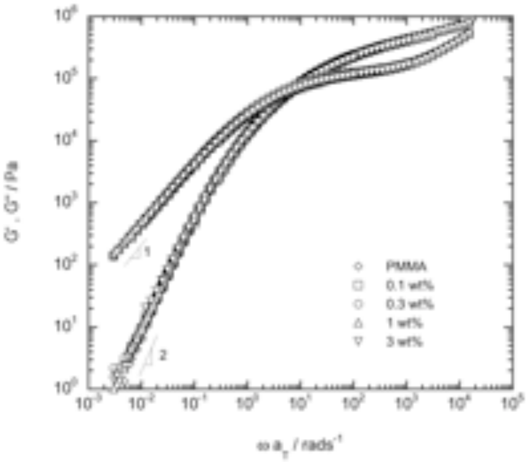


Figure 5. Mastercurves of storage modulus (*G'*) and loss modulus (*G"*) of PMMA and PMMA blended with fluorinated hyperbranched polymer at reference temperature of 190°C.

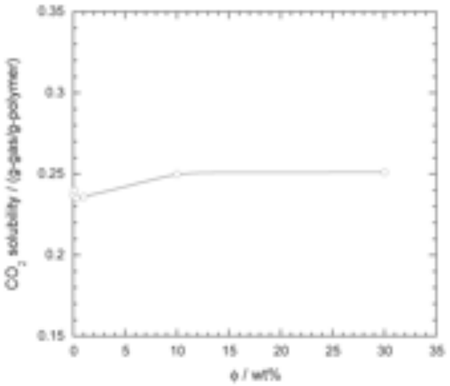


Figure 6. Effect of concentration of HBP-1 on the solubility of PMMA/HBP-1 blends at 15 MPa of CO_2 and 50°C.

Effect of Solubility of Gas on the Foaming

As discussed already, the solubility of gas has strong effect on the polymer foaming. It has been reported that fluorinated block copolymer provided nanocells generated in the segregated fluorinated domains due to the high affinity to CO_2 [6]. In this study, the solubility of CO_2 was examined by variation of weight with the amount of HBP-1 after saturation of gas at 15 MPa and 50°C. Figure 6 shows weight ratio of dissolved CO_2 to PMMA/HBP-1 blends. The solubility of PMMA was 0.24, which agreed with literature [7]. There was little change below 1 wt% of HBP-1. Even for excess addition of HBP-1 a slight increase of solubility was observed at 10 wt%, followed by saturation above it. PMMA has high affinity with CO_2 due to the interaction of carbonyl group with CO_2. We consider that the reason why the difference of solubility was observed attributes to the original properties of high solubility of CO_2 of PMMA.

Effect of Fluorination of Hyperbranched Polymer

The apparent increase of CO_2 solubility of PMMA/HBP-1 blend was not observed even at high concentration of HBP-1 as shown in Figure 6. In order to discuss the effect of the fluoride group in the hyperbranched polymer, we prepared the non-fluorinated hyperbranched polymer (HBP-2) which had similar chemical structure and molecular architecture as HBP-1 except no fluoride groups. Figure 7 shows SEM images of PMMA blended with HBP-2 of 0.1 and 0.3

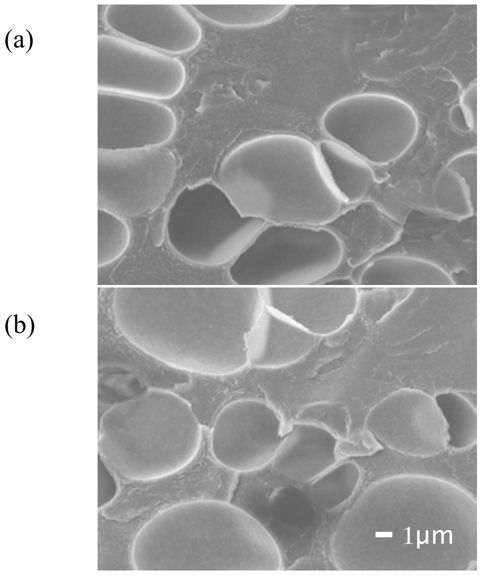


Figure 7. Scanning electron micrographs of the cross sections of (a)PMMA/HBP-2 (0.1 wt%) and (b) PMMA/HBP-2 (0.3 wt%) at 50°C. As for neat PMMA, see Figure 1(a).

wt%. As for neat PMMA, see Figure 1 (a). By comparing Figure 1 and 7, the difference between HBP-1 and HBP-2 is distinctly obvious. For PMMA/ HBP-2 system, the diameter of cell became large and number of cell density was decreased, though the impact was not so remarkable comparing with the influence of HBP-1. From the results of foaming PMMA with non-fluorinated polymer, we can say that the fluorinated group existed on near the surface of dendritic polymer plays important role as a nucleation sites. Fluoride compounds generally have high affinity to CO_2. We observed cryogenic fractured surface of PMMA/HBP-1 blends. In case of incompatible blends, domains can be observed due to segregated weak boundary. However, for PMMA/HBP-1 voids due to the domains was not observed in the fractured surface. This means the high compatibility between them and good dispersion of fluorinated hyperbranched polymer. This provides the high efficiency to generate numerous nuclei. We can say that the dispersed hyperbranched polymer reduced the free energy barrier to form nuclei and enhanced the nucleation rate. Although there was little change in solubility of PMMA/HBP-1 systems, the fluorinated group which has high affinity to CO_2 plays a key role in PMMA foaming.

Conclusions

We studied foaming of PMMA incorporated with various concentration of the hyperbranched polymer in which end groups were fluorinated were foamed by using $scCO_2$. Fluorinated HBP-1 exerted remarkably clear effect on the cellular structure of PMMA even at a very low amount of 0.01 wt%. At the low loading, a tail in the size distribution was observed. Increasing content lowered large cell fraction leading to the small average cell size (0.34 μm at 0.3 wt%) and 3 decade increase of cell number density. At 0.3 wt% the cell size and cell density showed minimum and maximum, respectively. There was little change in the dynamic viscoelasticity of PMMA/HBP-1. Variation of foaming behavior could not be related to the rheology of PMMA/HBP-1. Furthermore, change of the solubility of PMMA/HBP-1 was not confirmed below 1 wt% of HBP-1. The non-fluorinated HBP-2 consisting of similar structure to HBP-1 contributed not at all to the small cell and high cell density. Fluorination of hyperbranched polymer decreases the free energy and reduces the critical nucleus radius. HBP-1 showed high compatibility with PMMA up to several weight percentages. These factors resulted in the small cell size and increased cell density.

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