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ON FOAMING PROCESS OF VULCANIZED RUBBER USING PHYSICAL BLOWING AGENT

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ABSTRACT

In this paper, foaming process used supercritical carbon dioxide as a physical blowing agent and the characteristics of the foamed silicone rubber, which is vulcanized rubber, were investigated. First, the degree of vulcanization of silicone rubber was evaluated by the plasticity. And the relationship between plasticity and foaming conditions was investigated using samples changed variously degrees of vulcanization. Foaming process of vulcanized rubber was designed based on plasticity of rubber and discussed. And besides, the characteristics of foamed rubber were also measured. As results, foamed rubbers having fine cell size were produced using carbon dioxide as a physical blowing agent.

Keywords: process design, foaming process, vulcanized rubber, physical blowing agent, supercritical fluid.

1 INTRODUCTION

Foamed rubbers are used widely for many fields, such as roll portions of a printer or a copy machine, automotive parts, and building materials and so on. There are vulcanized rubber, thermosetting resin, etc. as cross-linked resins. It becomes three-dimensional network structure by applying heat etc. to those. Once it hardens, re-processing is difficult and foaming is also difficult. Foaming of rubber is widely formed by the chemical foaming technology. Chemical blowing agents cause to environmental pollution and to harm of human health. The foaming technology of foamed plastics with fine cell size by using carbon dioxide and nitrogen as a physical blowing agent, which is called Microcellular Plastics (MCP), is zealously examined now. The foaming technology of MCP, which uses the carbon dioxide generated by the oil refinement etc. as blowing agent, improves the environmental problem by chemical blowing agents [1-8].

On the foaming of the cross-linked resin such as a rubber, the balance of the growth of the cell and the progress of the cross-linking is important. The foaming and vulcanizing of vulcanized rubber simultaneously progress in chemical foaming technology, which reactive gas is generated by heating. But the simultaneously control of foaming and vulcanizing is difficult in physical foaming technology, which foaming and vulcanizing progress separately. As the cause, chemical reaction of unvulcanized rubber shows time and temperature dependence, and it bridges by applying heat etc., three-dimensional structure is formed, and it is raised that physical properties, such as a rate of elasticity, plasticity, and the degree of vulcanization, change in connection with it [9-10].

In this paper, foaming process used a physical blowing agent such as carbon dioxide and the characteristics of the foamed silicone rubber, which is vulcanized rubber, were investigated. First, the degree of vulcanization of silicone rubber was evaluated by the plasticity. And the relationship between plasticity and foaming conditions was investigated using samples changed variously degrees of vulcanization. Foaming process of vulcanized rubber was designed based on plasticity of rubber and discussed. And besides, the characteristics of foamed rubber were also measured.

2 DESIGN OF FOAMING PROCESS

Figure 1 shows schematic view of the relationship between degree of vulcanization and foaming of rubber. Longitudinal axis of this figure indicates plasticity, which means degree of vulcanization and horizontal axis indicates temperature or time. In this figure, region I is in the insufficient state of vulcanization which foaming progresses too much. Since this region is in the state where vulcanization is almost not progressing, plasticity of rubber is low and cells can not be held and are breaded and crushed after foaming. It is easy to become the foamed rubber with open cells and repulsive force becomes low. Region III is in the poor foaming state because vulcanization progresses too much. Since vulcanization progresses too much in this region, plasticity of rubber becomes very high and cells can not generate and grow. Region II is in the ideal state which foaming and vulcanization progress simultaneously while these maintain balance. In chemical foaming technology, since reactive gas generates and vulcanization progresses by heating, the state of region II can be realized comparatively. But this chemical foaming serves as a type of coupled design.

Since vulcanization and foaming are separately controlled by the physical foaming process, if vulcanization of the sample before foaming advances too much, the shortage of foaming will arise, and if vulcanization is weak, poor foaming will arise. Then, foaming process in consideration of the balance of vulcanization and foaming was devised which vulcanization was adjusted before foaming and it foams according to the degree of vulcanization after that. Figures 2 and 3 show two kinds of foaming process of vulcanized rubber by using physical blowing agent designed in this study. Figure 2 shows foaming process that vulcanization is progressed before soaking gas as blowing agent. That is, first, the plasticity is controlled by pre-curing before blowing agent is soaked and blowing agent is supplied into sample under temperature which vulcanization dose not progress. After blowing agent reaches saturation, foaming is carried out by decompression and post curing was done to keep the cell finally. This method is named process A in here.

Figure 3 shows another foaming process. That is, first, the blowing agent is soaked into the sample at the

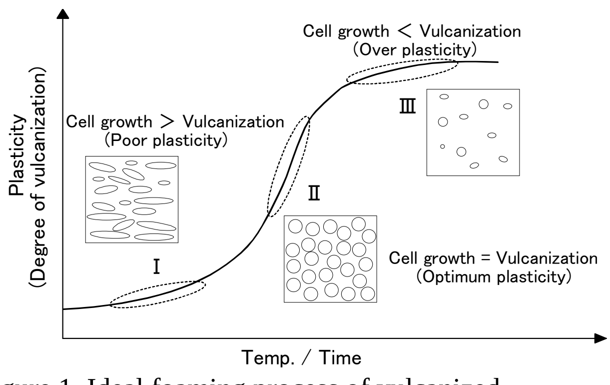

Figure 1. Ideal foaming process of vulcanized rubber considering plasticity.

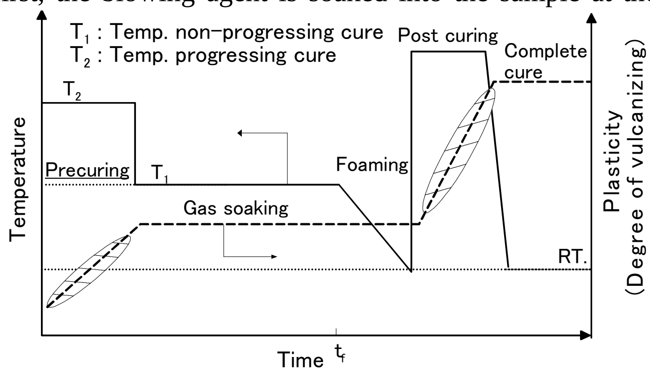

Figure 2. Foaming process progressed cure before gas soaking (Process A).

temperature that does not progress vulcanization. Next, it is controlled so that the plasticity is suitable for foaming through middle curing. After that, foaming is carried out by decompression and post curing was done to keep the cell finally. This method is named process B in here. It is thought that the forming of rubber which was able to balance vulcanization and foaming as shown in region II of Fig.1 is possible by such process. And these processes may serve as a type of decoupled design.

3 EXPERIMENTAL SETUP

3.1 MATERIALS

The material used in this research is unvulcanized silicone rubber (Shin-Etsu Co. Ltd.).

3.2 VISCOELASTIC BEHAVIOR

The viscoelastic behavior was measured to decide the plasticity and foaming conditions of the silicone rubber. Storage modulus was measured by compression mode in the range of 25 °C to 200 °C under constant frequency 1 Hz, using a viscoelastic analyzer (RSA-III; Rheometric Scientific F.E.Ltd.).

Figure 4 shows the temperature dependence of the storage modulus of the unvulcanized silicone rubber. As shown in this figure, it turns out that elasticity of silicone rubber rises in the range of 90 °C to 110 °C. It is thought that the plasticity of the silicone rubber used in this study may control in the range of 90 °C to 110 °C. As results, it can be predicted that is necessary to control the temperature within the range of80 °C to 100 °C, which

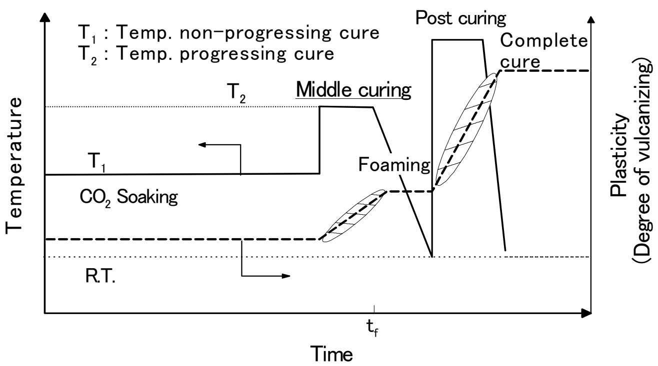

Figure 3. Foaming process progressed cure with gas soaking (Process B).

are pre-curing, soaking of blowing agent, and middle curing of the silicone rubber.

3.3 PLASTICITY

The change of the plasticity with various temperatures was measured based on viscoelastic behavior shown in Figure 4 and the plasticity during foaming process was estimated.

Figure 5 shows time dependence of the plasticity when the silicone rubber is cured at the temperature of 80 °C, 90 °C, and 100 °C. This figure was made as the

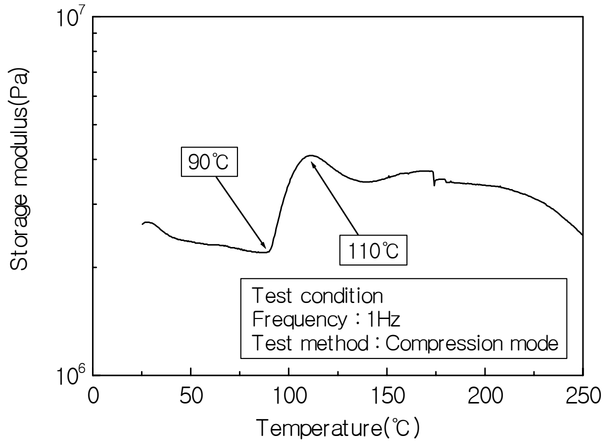

Figure 4. Viscoelastic behavior of unvulcanized silicone rubber.

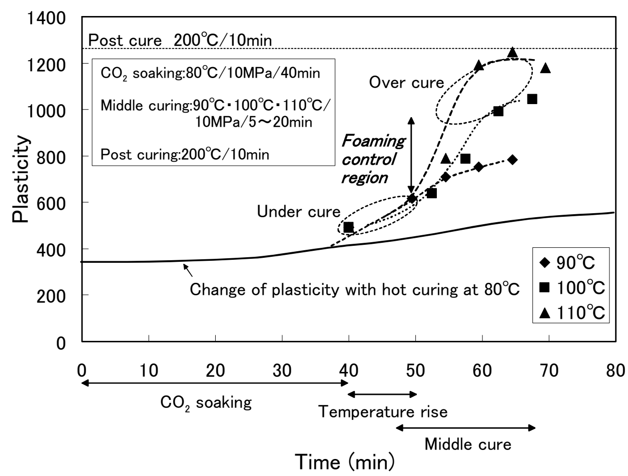

Figure 5. Estimation of plasticity with temperature.

plasticity of silicone rubber at 90℃ and 100 °C was shifted to that of 80 °C/40 min, in order to estimate plasticity of process B. As shown in this figure, it turns out that the plasticity of the sample is to be able to change variously by heating. In a word, it seems that the sample used in this study is possible to foam by controlling the plasticity within the range of 600 to 1000.

3.4 FOAMING METHODS

The foaming experiment was carried out by the batch foaming system, and carbon dioxide was used for the blowing agent. The batch foaming system is a method that blowing agent is soaked under high pressure, and is foamed by decompression. It is difficult to control simultaneously foaming and vulcanization of unvulcanized rubber by using this method. Therefore, foaming experiment carried out by two methods based on processes shown in Figsures 2 and 3 using batch system.

Figure 6 shows forming system and foaming conditions. Figure 6 (a) shows process A and (b) shows process B based on processes shown in Figsures 2 and 3. In process A, first, the plasticity was controlled in the range of 400 to 1000 that seems to be able to foam, under the conditions of 80 °C to 100 °C and 10 min. to 40 min. using electric oven. And blowing agent was supplied into sample under the conditions of 80 °C / 10 MPa / 1 h which vulcanization dose not more progress using pressure vessel. After blowing agent reached saturation, foaming was carried out by decompression and post curing was done to keep the cell finally under the condition of 200 °C / 10 min. using electric oven.

In process B, first, the blowing agent was soaked into the sample under the condition of 80 °C / 10 MPa / 40 min. that vulcanization does not progress, using pressure vessel. Next, as middle curing, the blowing agent was soaked into sample under the condition of 90 °C to 110 °C / 10 MPa / 5 min. to 20 min., which vulcanization progresses, and plasticity was changed by it. After blowing agent reached saturation, foaming was carried out by decompression and post curing was done to keep the cell finally under the condition of 200 °C / 10 min. using electric oven.

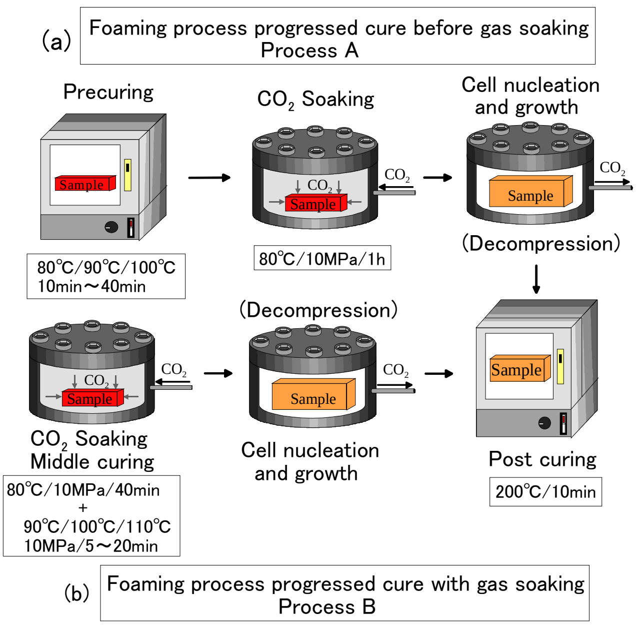

Figure 6. Experimental foaming process and conditions.

4 RESULTS AND DISCUSSION

Figure 7 shows micrographs of foamed silicone rubber obtained in this study comparing with chemical foaming. Figure 7 (a) is photograph foamed by the process A and (b), (c) are photographs foamed by the process B. As shown in figures (a), (b), cell sizes of foamed silicone rubber obtained in this study become

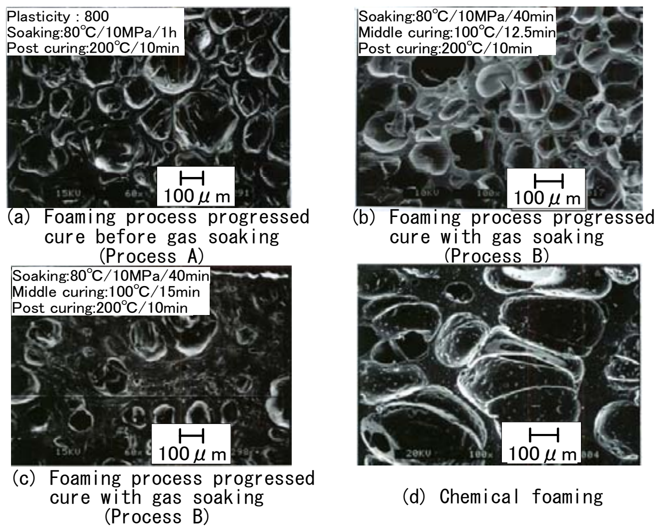

Figure7. SEM micrographs of foamed silicone rubber at various foaming processes.

small compared with that of chemical foaming shown in (d). But as shown in (c), when middle curing is lengthened, poor foaming will be raised. It is thought that plasticity becomes high and foaming was prevented. These results show that fine cells can be introduced by controlling the plasticity.

Figure 8 shows the relationship between average cell size, cell density and plasticity of foamed silicone rubber by foaming processes A and B. Average cell sizes decrease with an increase in plasticity and cell densities increase with an increase in plasticity in both processes. This tendency is remarkable in the case of process B. And cell size is small and cell density is high compared with that of chemical foaming shown in this figure. Also in the same plasticity, cell size is so small that middle curing temperature in process B is high, and cell density has increased. As this reason, since middle curing temperature is high, it is thought that the solubility of blowing agent was promoted and initial number of cells produced at the time of decompression increased

Figure 9 shows the relationship between elastic modulus and plasticity of foamed silicone rubber by foaming processes A and B. The elastic modulli increases with an increase in plasticity in both processes. And these modulli are high compared with that of chemical foaming as shown in this figure. Also in the same plasticity, elastic modulus by process A becomes little high compared with that by process B. As this reason, it is though that skin layer is created a little on the surface of specimen by process A. In process B, elastic modulus of specimen by middle curing temperature 100 °C is high compared with that of 90 °C. This reason is though that foamed specimen by middle curing temperature 100 °C has small cell size compared with that of 90 °C.

Figure 10 shows the relationship between hardness and plasticity of foamed silicone rubber by foaming processes A and B. The hardness increases with an increase in plasticity in both processes. Also in the same plasticity, hardness by process A becomes little high comparing to that by process B. As this reason, it is though that skin layer is created a little on the surface of specimen by process A.

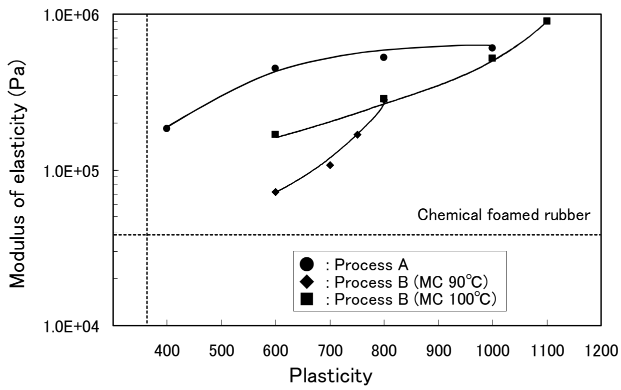

Figure 9. Relationship between modulus of elasticity, specific modulus and plasticity of foamed silicone rubber.

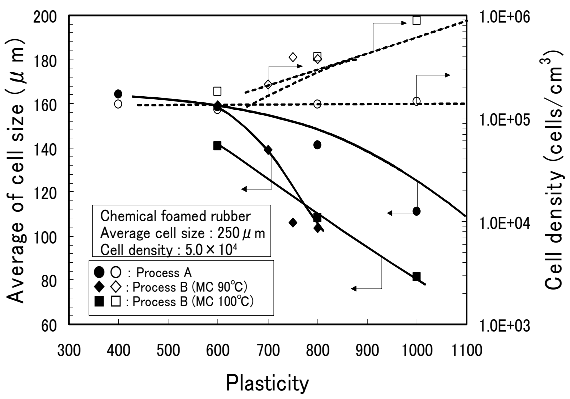

Figure 8. Relationship between average cell size, cell density and plasticity of foamed silicone rubber.

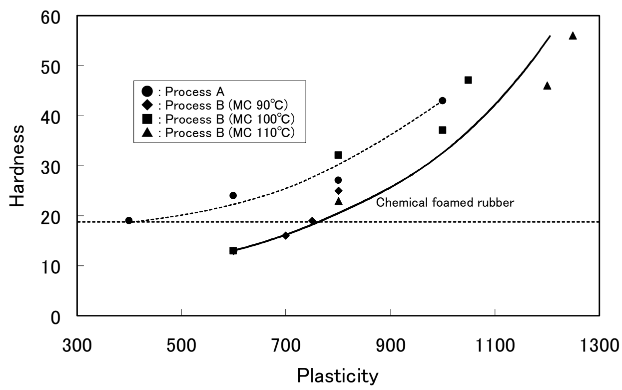

Figure10. Relationship between hardness and plasticity of foamed silicone rubber.

5 CONCLUSION

Foaming process used carbon dioxide as a physical blowing agent and the characteristics of the foamed silicone rubber, which is vulcanized rubber, were investigated. The following results were obtained.

1. The balance of foaming and vulcanization was controllable on the basis of the degree of plasticity.
2. Foaming processes of vulcanized rubber were designed based on plasticity of rubber.
3. The foamed rubber which has cell size 100 micro-meters or less more detailed than the conventional chemistry foamed rubber has been formed using the devised foaming processes.
4. By controlling the degree of plasticity of sample, the internal structure and the mechanical property of foamed rubber were controllable.

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