Foaming Mechanism of Perfluorocarbon-Polymer in Extrusion Process

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We are developing coaxial cables used in cellular phone base stations. To obtain cables with demanded electric properties, fine and uniform foaming is critically important. We used a perfluorocarbon polymer appropriate for this application to compare foaming techniques. Although technology to make fine and uniform foams is very important, there are few scientific works on foam processing. We analyzed it using an original method for representing the state of foaming under various conditions and investigated the foaming mechanism during extruding process. Using these analyzed data, we made foam with more than 70% degree of foaming.

1. Introduction

In recent years, the frequency used in cellular phones is shifting into high frequencies and therefore, the signal attenuation by insulator is also increasing. Hence, there is much demand for materials with low dielectric-loss. Furthermore, the coaxial cables used in cellular phone base stations carry a tremendous amount of power and may heat beyond 100°C when operated at high frequencies. Therefore, high temperature resistance is also required. Perfluorocarbon polymers are materials that meet such requirements as dielectric properties and melting point. To reduce attenuation further, it is necessary to foam the insulator. Less signal attenuation and fine foaming make it possible to reduce the diameter of the cables and the size of the base stations.

To develop cables with stable, low attenuation, and high-heat resistance properties, we investigated the mechanism of extrusion foaming process using hexafluoropropylene-tetrafluoroethylene copolymer (FEP), which is one of the perfluoropolymers that can be melt-extruded. Using the analyzed data, we examined a high degree of foaming of more than 70%.

2. Experimental

2.1. Material

Perfluoropolymers include polytetrafluoroetylene (PTFE), hexafluoropropene-tetrafluoroetylene copolymers (FEP), and perfluoroalkylvinylether-tetrafluoroetylene copolymers (PFA). PTFE has the lowest dielectric properties among them but cannot be processed by continuous melt-extrusion, whereas lamb molding used for PTFE provides the shorter cables than the extrusion. We chose FEP and PFA as candidate compounds for analysis because of processing issues, as continuous melt processing can be conducted on FEP. In this report, we show our experiment on FR5030 sold by DuPont as the compound for extruding process. Nitrogen gas was used for foaming and was injected as a supercritical fluid.

2.2.Measurement of dielectric properties

Perfluoropolymers include polytetrafluoroetylene (PTFE), hexafluoropropene-tetrafluoroetylene copolymers (FEP), and perfluoroalkylvinylether-tetrafluoroetylene copolymers (PFA). PTFE has the most favorable dielectric properties (Fig. 1), but cannot be processed via melt-extrusion; so long cables cannot be continuously produced. We chose FEP as a candidate for analysis because of processing issues, since continuous melt processing can be conducted on FEP. In this report, we experimented on FR5030 sold by DuPont as compound for extruding process.

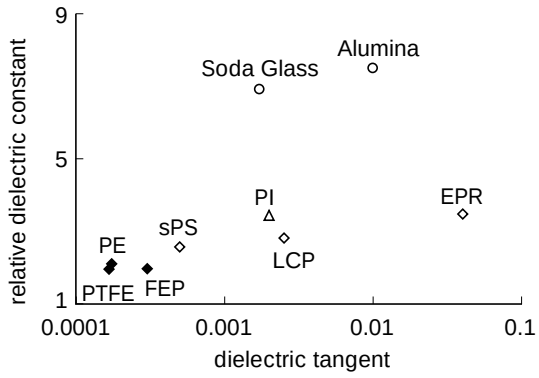

Fig.1. Dielectric properties at 2.45 GHz.

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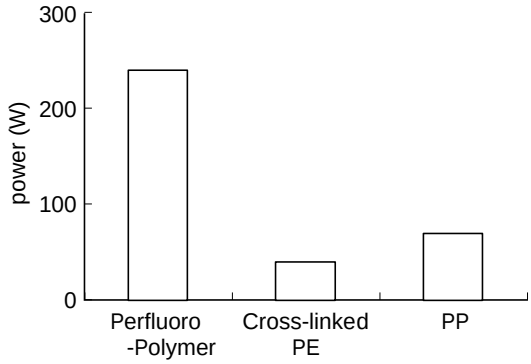

Fig.2. Allowable power.

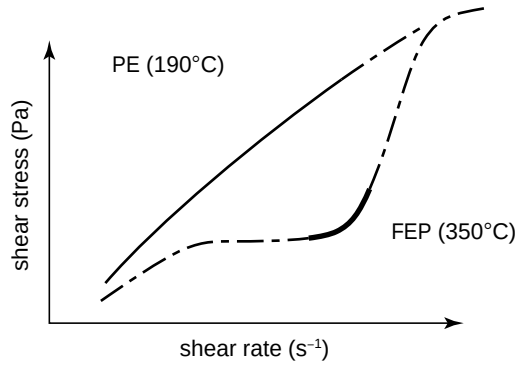

Fig.3. Shear rate - shear stress conceptual plot.

Nitrogen gas was used for foaming, and was injected as a supercritical fluid.

2.3 Transmitting power capacity

Transmitting power capacity of cables depends on the heat resistance of the dielectric polymer. A high melting point leads to an increased transmitting power which is desirable. The power capacity of polyethylene, polypropylene, and perfluorocarbon polymers are compared in Fig. 2.

3. Extrusion foaming

3.1. Processing method

In general, cable insulators are continuously extruded because of productivity issues, and this is the case with FEP and PFA. However, FEP and PFA are coated on a wire conductor by a method different from that of the generic polyolefins such as polyethylene. Polyethylene is drawn with a pressure dye, but FEP is drawn with a tubing dye. The reason comes from the shear properties of perfluorocarbon polymers. A conceptual plot of shear stress versus shear rate is shown in Fig. 3, where melted polyethylene and melted FEP are compared. The state where the melt-extruded material has a smooth surface is called the normal region (solid line in Fig. 3), and the state where melt fracture occurs is the overshear region (dotted line in Fig. 3). In polyethylene, the normal region covers a wide range of shear rate. On the contrary, the normal region of FEP is very narrow, covering only low shear rate, and quickly enters the overshear region. However, when the shear rate is increased further, the drawn FEP has a smooth surface and looks like those from the normal region. This region is called the supershear region (thick line in Fig. 3). It is important to extrude FEP in this region.

The radius of the pressure die to be used is slightly smaller than the target insulator radius, and so it is in the high shear region. Polyethylene is very much in the normal region under this condition, but FEP in the supershear region easily enters the overshear region at low line speed; therefore, it is very difficult to draw without the occurrence of the melt fractures. Extrusion in the normal region is virtually impossible as the line speed must be significantly decreased to accomplish this.

On the contrary, the die radius of the tubing die can be changed; and thus the shear speed can be matched to realize the supershear region. Therefore, tubing dies are used for extrusion of perfluorocarbon polymers like FEP. The melted resin is extruded much more in the case of a tubing die than that of a pressure die, and the extruded resin should be drawn to cover copper wire conductor. Therefore, it is important to appropriately set the ratio of resin cross-section just after drawing to the resin cross-section after coating. This ratio is called Draw-Down Ratio (DDR) [1]. The region between the die end and the start of the wire to be coated is usually called the cone, as the stretched resin looks like a cone.

3.2. Extruding line

The adjustable parameters are resin temperature (from melting of resin and gas injection to cross-head), line speed, conductor heat, cooling temperature and vacuum pressure when drawing from the tubing die. Of these parameters, it is known that the state of foaming depends largely on the line speed and the vacuum pressure when drawing from the tubing die [2].

The sizes of the tubing die and the nipple were selected as follows :

(1) The shear rate-shear stress curve is obtained with a capillary rheometer, and the shear speed range of the supershear regime is estimated.
(2) The target line speed and the amount of the extruded resin are determined.
(3) A few sets of dies and nipples whose radii matches the shear rate obtained in the first step are fabricated.
(4) The appropriate DDR and DRB are selected from these combinations.

DRB : Contraction form of “Draw Ratio Balance” described as following formula.

Table 1. Comparison of methods.

Item	Amount of gas per unit amount of resin	Shear speed with die	Weight per unit wire
(1)	High possibility of change with condition → High possibility degree of foaming and state of foaming will change	High possibility not in supershear region	Unchanged
(2)	Unchanged as always fixed	Unchanged	Change greatly → Large effect from outer radius

$$DRB = (D_d / D_n) / (D_{core} / D_{cond})$$

D_d : a diameter of die
D_n : an outside diameter of nipple
D_{core} : an outside diameter of insulator
D_{cond} : a diameter of conductor

3.3. Extruding

We tried various conditions of the extrusion line to obtain good foam. This report is focused on the correlation between the line speed and the state of foaming, and the results are summarized.

To understand the relation between the line speed and the state of foaming, we made foam with the same degree of foaming with each line speed. These two methods were considered.

Method (1): Adjust the amount of the resin coated on the unit length of a wire and the amount of gas for each line speed.

Method (2): Fix the amount of gas and discharge rate and change only the line speed.

We experimented and compared the two methods and then summarized the results in Table 1. In method (1), some drawn amounts (resin flux) were not in the supershear region, so the wire could not be coated. Therefore, it was difficult to compare the results when line speed was changed. On the contrary, in method (2), there was a limit to the line speed as the thickness affected the quality when the line speed was increased, but the results could be compared.

3.4. Analysis of foam

In general, the state of foaming on the cross-section of the insulator is observed and analysis is conducted with cell radius and cell density as parameters. However, the analysis of the foam fabricated with this tubing die could not describe the intrinsic state of foaming. To describe the intrinsic state of foaming and to understand the foaming mechanism, we analyzed the longitudinal section of the insulators. On conducting the analysis, we realized that the shape of the cell should be considered, and hence, we included the aspect ratio of the cell as a parameter.

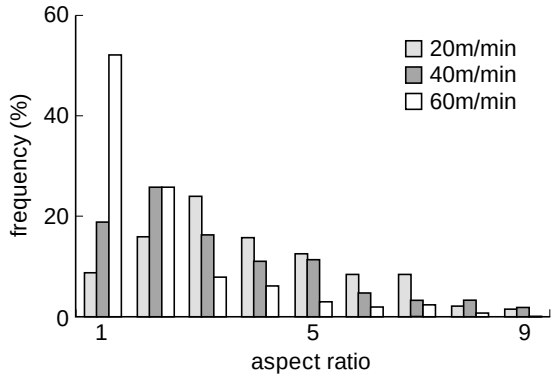

Fig.4. Line speed and aspect ratio.

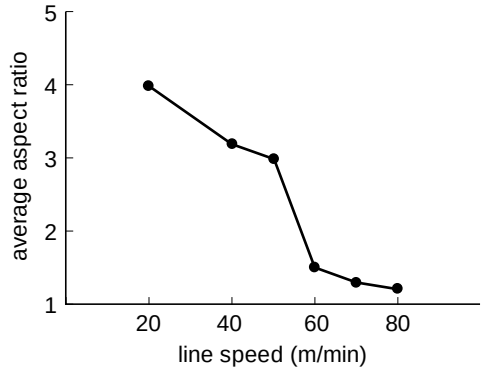

Fig.5. Line speed and average aspect ratio.

The drawn foam is usually longer in the longitudinal direction, so the aspect ratio was defined as the ratio of the cell length in the longitudinal direction to the diameter.

To analyze the cell shape, the cell radius, and the cell cross-section area, the cross-section was observed by scanning electron microscope (SEM). The cell images were fed into a computer, and were digitalized and statistically analyzed.

4. Results and discussion

Figure 4 shows the relationship between the line speed and the foam cell shape. The vertical axis represents the frequency and the horizontal axis represents the average aspect ratio of the cell length in longitudinal direction and the diameter.

When the ratio is close to 1, the cell is close to a perfect sphere, and when the ratio is greater, the cell is prolonged in the longitudinal direction. When the histogram of the aspect ratio is compared for each line speed, the peak of the histogram shifts to the lower side 1 with line speed increased. To understand this relation, it is necessary to consider the time from the release of melt-pressure to the start of foaming [3)-8)]. In general, there is some time before foaming starts and is reported in many literatures. If the time before foaming is constant, line speed is equivalent to the distance from the die to the onset of foaming. This distance from the die is very important, as FEP

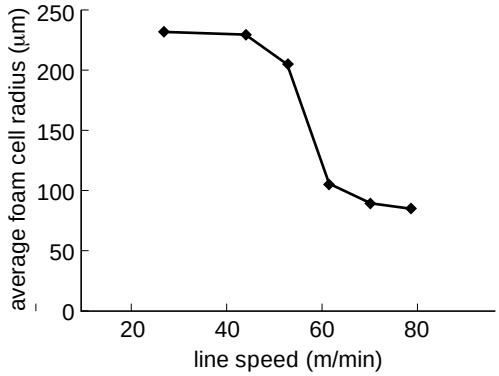

Fig.6. Line speed and standard deviation of aspect ratio.

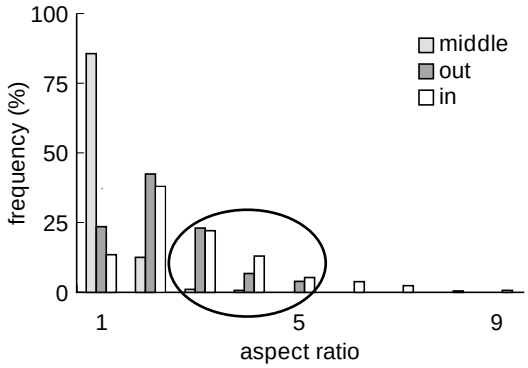

Fig.7. Aspect ratio of foam insulation in the direction of thickness (without skin layer, only foam layer).

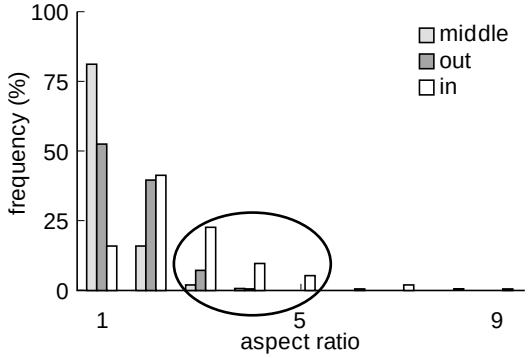

Fig.8. Aspect ratio of foam insulation in the direction of thickness (with skin layer, foam layer, and skin layer).

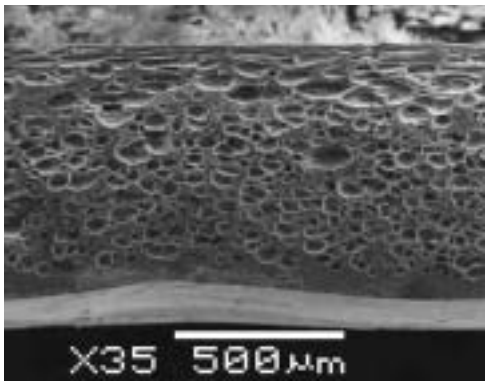

Fig.9. 50% degree of foam with skin.

is covered using a tubing die. When covering with a tubing die, the resin is stretched at the cone. When foaming starts in the cone, it can be assumed that the drawing of the resin and the stretching and growing of the foam cell happen simultaneously. Therefore, when foaming starts in the cone close to the die, the aspect ratio becomes larger. Thus, if the time before the foaming starts does not depend on line speed, after a specific line speed, the aspect ratio will be close to 1, and the distribution will be narrower. This assumption is reasonable for the following reason. The relation between average aspect ratio and the line speed is shown in Fig. 5.

There is a line speed where the relation between the aspect ratio and the line speed becomes discontinuous (critical line speed) and the aspect ratio converges to 1. Thus, even if the line speed is increased further, the fact is that the foaming that will start past the cone will not change and so the distribution of aspect ratio will not change. The transition of foam cell size is shown in Fig. 6. It can be seen that the foam cell radius becomes smaller at faster line speed, and follows a curve similar to the aspect ratio. The reason assumed to be is that the onset of foaming to the growth of the foam cell finishes in the short time after moving through the cone to cooling.

From these data, we can obtain an estimate of the critical line speed and cone length and thus estimate the time before foaming. In this experiment, the estimated values of cone length and critical line speed were approximately 15 mm and 50 m/min, respectively. Therefore, the time before foaming was estimated at 18 ms (milliseconds).

Next, the insulator was separated into three regions with equivalent thickness, and the trend of aspect ratios in each region was shown in Fig. 7 as a histogram. Foam cells with low aspect ratio appear in the middle of the foam, regardless of the line speed.

The following are the likely reasons.

In general, unlike low molecular weight fluids, melted polymer is a non-Newtonian fluid and swells when extruded from a die. Therefore, there is a stress normal to the extruding direction. So, the surface of insulation is decompressed faster than the middle layer. In this case, the foaming starts from the surface, so the surface is more likely to start foaming at the cone. When the skin layer is pressed simultaneously along with those surrounding the foam layer, the foam layer is comprised of all spherical foam cells on the side of the skin layer, and prolonged foam cells appeared only on the conductor side. The results are shown in Fig. 8 as a histogram, and the cross-sections are shown in Fig. 9.

From these results, we expect the form will be

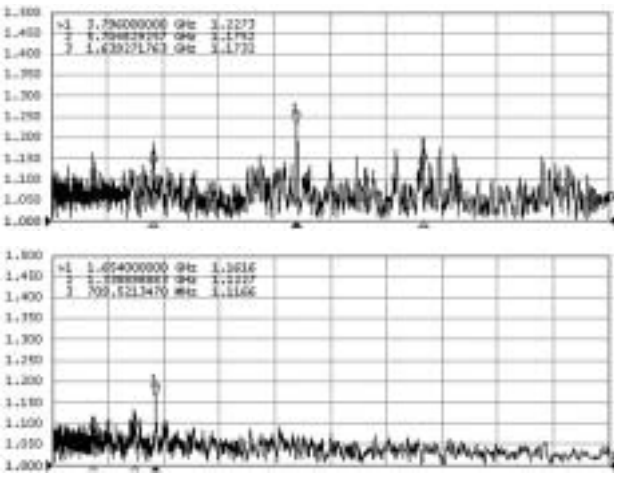

Fig.10. VSWR of foam insulation with huge cell (above) and fine cell (below).

composed entirely of spherical foam cells if the inside skin layer can also be extruded simultaneously.

5. Cable

By optimizing drawing conditions using the above data, we fabricated an insulator with 50% degree of foaming and in the desired state. The longitudinal section is shown in Fig. 9. A corrugated tube was attached to this insulator to complete the coaxial cable. As a result, we obtained very low attenuation and voltage-standing wave ratio (VSWR) as shown in Fig. 10. The longitudinal sectional photograph without skin layer is shown in Fig. 11 and the photograph with skin layer in Fig. 9.

We also fabricated an insulator with 75% degree of foaming, though the state of forming was somewhat imperfect. A picture is shown in Fig. 12.

6. Conclusion

We investigated the foaming mechanism in a continuous drawing process by analyzing the state of foaming at various conditions.

We were able to explain as to why the state of foaming greatly changes with line speed by considering the time between decompression and to the start of foaming. When the foam layer is drawn by itself, it is more likely that the foam cell is prolonged at the surface and near the conductor. This problem was resolved by simultaneously drawing a skin layer.

Finally, we have realized a good state of foaming at

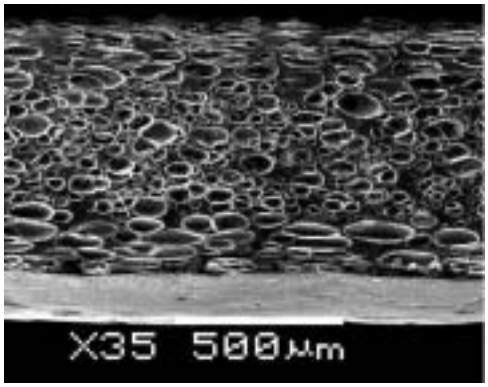

Fig.11. 50% degree of foam without skin.

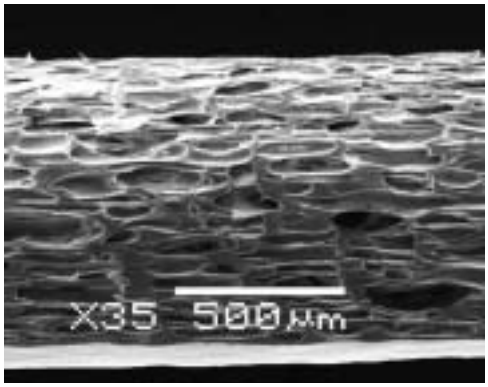

Fig.12. Insulation with 75% degree of foaming.

50% degree of foaming. Our goal is to increase the degree of foaming, and right now we have achieved 75% degree of foaming.

References

1) "Fussojushi" published by Nikkankougyousha (in Japanese)
2) U.S. Patent 134164, 1987
3) T.Miura, et.al.: IEICE Trans. Electron., Vol.E77-C, No.6, pp.900-907, 1994
4) Japan Society of Polymer Processing Annual meeting '02, II-208, p.99, 2002
5) Japan Society of Polymer Processing Annual meeting '03, II-109, p.91, 2003
6) Japan Society of Polymer Processing Annual meeting '03, II-202, p.109, 2003
7) Japan Society of Polymer Processing Sympo.'04, G107 p.123, 2004
8) "Jushi no happouseikeigijutsu" published by Gijutsujouhoukyoukai (in Japanese)