Nano-Composite Heat-Shrinkable Tubing

Satoshi YAMASAKI*, Shinya NISHIKAWA, Hiroshi HAYAMI, Hayato AOI, Ryouhei FUJITA and Tomoyoshi KISHIMOTO

Sumitube is heat-shrinkable tubing that is widely used in the electronics, automotive, aerospace and other industries for insulation protection and waterproofing of electric wire terminals or harnesses, bundling electric wires, insulation protection of electronic parts or components, and corrosion protection of metal pipes. Recently, thinner wall heat-shrinkable tubing is required for the purpose of saving space and weight, especially for applications involving electronic parts and components. However, thinner wall tubing generally causes difficulty in covering electronic parts due to its lack of rigidity. Therefore, we have developed a very thin wall heat-shrinkable tubing by applying polymer nano-composite technology (nano-meter size fillers dispersed in polymer), which has sufficient rigidity for easy handling, positioning, and installation over electronic parts or components and shrinks in less time, at a lower temperature.

Keywords: heat-shrinkable tubing, electron beam irradiation, polymeric material, cross-linking, polymer nano-composite technology

1. Introduction

Heat-shrinkable tubing, which shrinks to a pre-determined diameter when heated, is widely used in the electronics, automotive, aerospace and other industries for insulation, mechanical protection, environmental sealing of electric wire terminals or harnesses, bundling electric wires, insulation protection of electronic parts or components, and corrosion protection of metal pipes.

Since 1964, Sumitomo Electric Industries, Ltd. has been manufacturing and marketing heat shrinkable tubing under the trade name of Sumitube. Heat-shrinkable tubing having a wall thickness of 200 µm or more with a shrink temperature of about 90 to 110˚C has conventionally been used in above mentioned technical fields. However, customers often require thinner wall heat-shrinkable tubing for the downsizing of electronic parts and a need to decrease weight.

Simple reduction of wall thickness does not satisfy such customer needs, since reducing wall thickness decreases the rigidity of tubing thereby causing difficulty during the installation of the tubing over the components. In order to solve this problem, the authors developed a new heat-shrinkable tubing with a very thin wall thickness featuring improved rigidity at the same time.

2. Method of Producing Heat-Shrinkable Tubing and the Principle of Shape Memory

2-1 Method of producing heat-shrinkable tubing

The manufacturing process of heat-shrinkable tubing is shown in **Fig. 1**. The process consists of three steps: extrusion, electron beam irradiation, and expansion. For example, polyethylene is extruded into a tubular shape using an extruder, and then is cross-linked(1) by a high energy electron beam*1 accelerator. Subsequently, the cross-linked

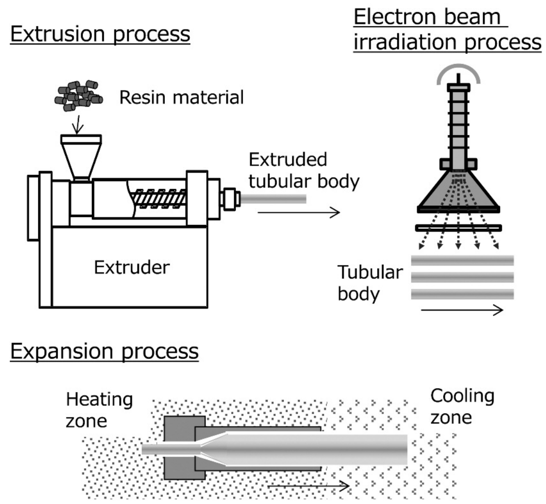


Fig. 1. Heat-shrinkable tubing production system

tubing is softened in the heating zone and expanded towards the radial direction by internal pressure or other means, and then cooled to fix the expanded shape as the final heat-shrinkable tubing product.

2-2 Principle of shape memory of heat-shrinkable tubing

The principle of heat-shrinkable tubing is shown in **Fig. 2**. Polyethylene is a crystalline resin*2 consisting of a crystalline area and amorphous regions. When electron beam irradiated, the crosslinking reaction occurs in the amorphous areas.

When the cross-linked polyethylene is heated at temperature above the melting point of crystalline area, the material becomes soft enough to be expanded, and when cooled, the expanded shape is retained by growth of the crystalline areas.

In contrast, when the expanded cross-linked polyethylene is reheated at a temperature above the crystalline

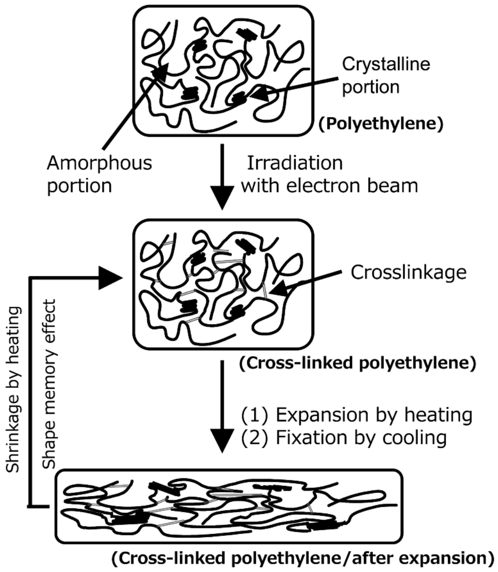


Fig. 2. Principle of heat shrinkage

melting point, the material is softened and shrinks to its original shape due to the cross-linked molecular chains of the amorphous area (shape memory effect).

3. Material for Producing Heat-Shrinkable Tubing

The shrink temperature of heat-shrinkable tubing depends on the melting point of the base resin material used. As shown in **Fig. 3**, heat-shrinkable tubing made of low density polyethylene (LDPE, melting point: 110˚C) completes the heat-shrinkage at a temperature slightly higher than 110˚C and recovers to its original shape before expansion.

Figure 4 shows the relationship between the melting point and elastic modulus of various types of polyethylene. This figure shows that the elastic modulus increases as the melting point increases. Since reducing the wall thickness of the tubing decreases its rigidity, it causes difficulty in positioning the tubing over the electronic parts or components. One solution for this problem is to use linear low density polyethylene (LLDPE), high density polyethylene (HDPE), or other high modulus polyethylene. However, high elastic modulus polyethylene requires higher shrinkage temperature due to high melting points. As a result, such polyethylene lowers heat shrink workability and might cause thermal damage to electronic parts or components.

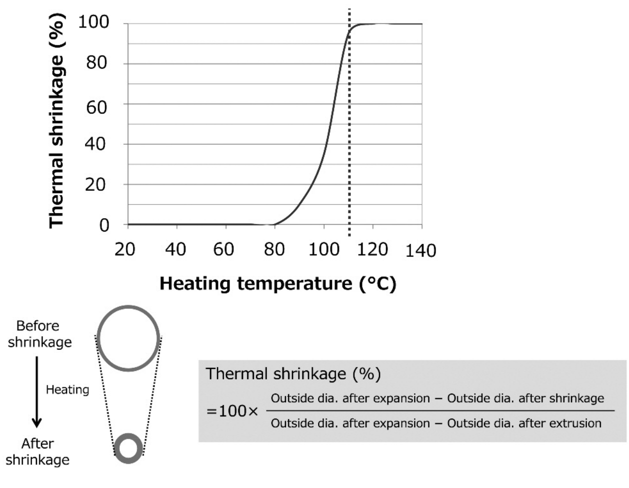


Fig. 3. Dependence of thermal shrinkage on heating temperature (Material: low-density polyethylene, mellting point; 110˚C)

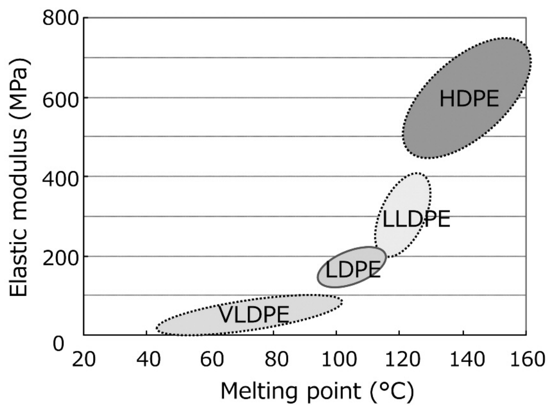


Fig. 4. Melting point and elastic modulus of several types of polyethylene

4. Development of New, Very Thin-Wall, Heat-Shrinkable Tubing

4-1 Objective of development and concept of material development

In this project, we developed a 50 μm thin-wall, heat-shrinkable tubing having a rigidity (which governs the ease of installation over electronic parts or components) and shrinkage temperature equivalent to those of conventional 200 μm thick-wall low-density polyethylene tubing products.

To achieve 50 μm thin-wall tubing with rigidity equivalent to that of 200 μm thick-wall low-density polyethylene tubing, the elastic modulus of raw material is calculated to be 300 MPa or more. Hence, we decided to develop a new low density polyethylene having a higher elastic modulus. One proven method of increasing the resin's elastic modulus is to disperse inorganic fillers or reinforcing materials. A typical example of reinforcing material is talc (hydrated magnesium silicate).

In this project, we focused on polymer nano-composite technology(2), which has been researched intensively in recent years.

The nano-composite material is a resin composite in which nanometer-size fillers are homogeneously dispersed in polymers. According to published papers, nanometer-size fillers have a larger surface area compared with conventional inorganic fillers. Therefore the addition of only a small amount of nanometer-size fillers can improve the physical or mechanical properties of polymers(3),(4).

We selected the layered silicate as a raw material for nanometer-size filler expecting the exfoliation of the layered silicate to occur during the melt mixing process with low-density polyethylene (**Fig. 5**).

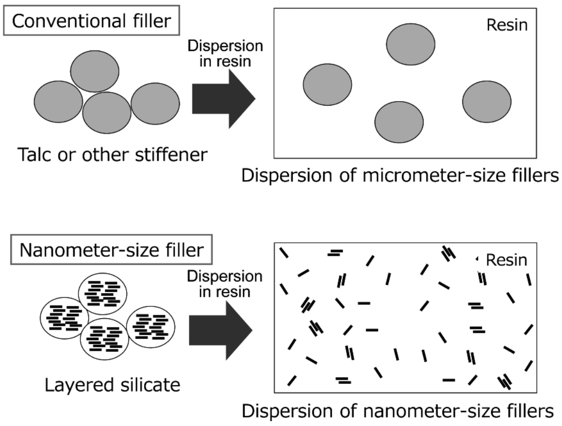


Fig. 5. Nano-composite materials

4-2 Evaluation of material

Two types of low-density polyethylene materials were prepared: one (specimen (1)) in which talc (primary particle size: 10-20 μm) was dispersed and another (specimen (2)) in which layered silicate (primary particle size: 10 μm) was exfoliated to make a polymer nano-composite. The results are shown in **Fig. 6**. Specimen (1) did not increase in elastic modulus, whereas specimen (2) showed almost two times higher elastic modulus compared with specimen (1) and exceeded the target value of 300 MPa.

The phase structure of specimen (2) was investigated using a transmission electron microscope (TEM). For the TEM observation, the specimen was stained with ruthenium, embedded in an epoxy resin, and cut into ultrathin slices with a microtome. A TEM image of the specimen is shown in **Photo 1**. This image shows that specimen (2) was a polymer nano-composite material in which approximately 200 nm-length, several nm-thick silicate plates were dispersed in polyethylene. We concluded that the reinforcing effect of nanometer-size fillers dramatically improved the elastic modulus of the low density polyethylene.

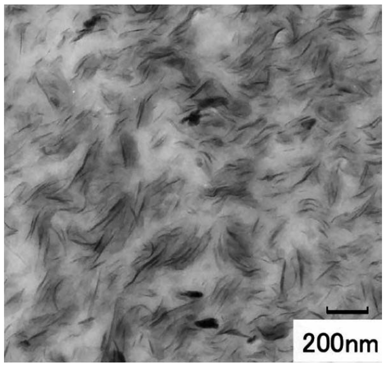


Photo 1. Transmission electron microscope photograph of specimen

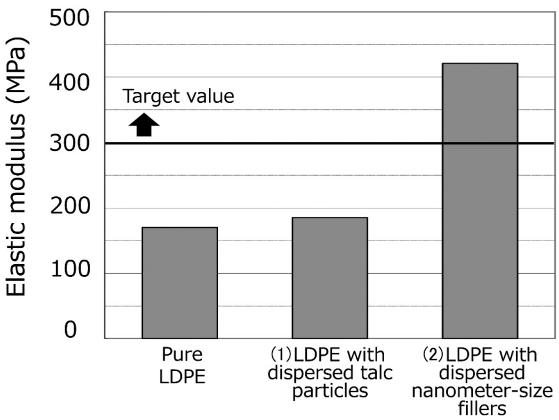
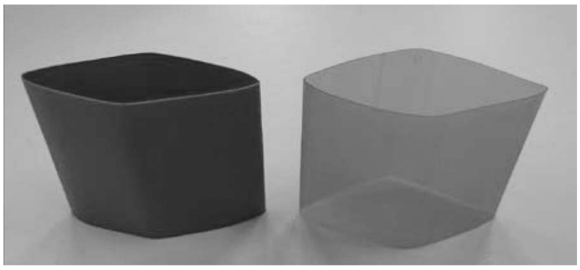


Fig. 6. Elastic modulus comparison results

4-3 Evaluation of test-manufactured heat-shrinkable tubing

A tubing with an inside diameter of 8.0 mm and wall thickness of 110 μm was designed and manufactured for test purposes by extruding the above-discussed low density polyethylene based nano-composite material. The extrusion proceeded successfully and a heat-shrinkable tubing (18 mm inside diameter and 50 μm final wall thickness) was obtained by electron beam irradiation and expansion.

The trial-manufactured heat-shrinkable tubing showed almost the same rigidity as conventional 200 μm thick tubing and was expected to facilitate similar ease of covering over electronic parts or components. This was confirmed by observing that the developed tubing has sufficient column strength to stand alone as illustrated in **Photo 2**.



Conventional tubing (Wall thickness: 200 μm) New tubing (Wall thickness: 50 μm)

Photo 2. Self-standing of conventional and new products

In addition to the improved rigidity, the trial-manufactured heat-shrinkable tubing satisfied general specifications listed below (**Table 1**).

When the tubing was heated to 110°C in an oven for one minute, the inside diameter of the tubing recovered to 8.0 mm, the same as the extrusion diameter, verifying that the heat-shrink characteristics are comparable to those of conventional tubing (18 mm inside diameter, 200 μm wall thickness) (**Fig. 7**).

Table 1. Evaluation results of new heat-shrinkable tubing

Item		Unit	Target value	New tubing	Conventional tubing
Wall thickness		μm	50±5	50±2	200±3
Shrinkage temperature		℃	≦ 110	105	100
Tensile characteristics	Elastic modulus	MPa	≧ 300	485	210
	Tensile strength	MPa	≧ 14	26	19
	Elongation	%	≧ 200	310	550
Retention of characteristics after heat aging at 140°C for 7 days	Tensile strength	%	≧ 50	96	95
	Elongation	%	≧ 50	81	94

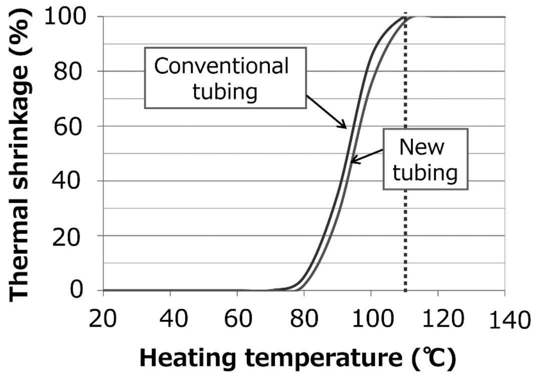


Fig. 7. Dependence of thermal shrinkage on heat temprature

It was also confirmed that the trial-manufactured heat-shrinkable tubing had reduced its heat capacity due to its thinner wall thickness, contributing to reducing the shrinkage time by approximately 10 seconds (**Fig. 8**). This will make it possible for an automatic shrinking machine to reduce overall processing time.

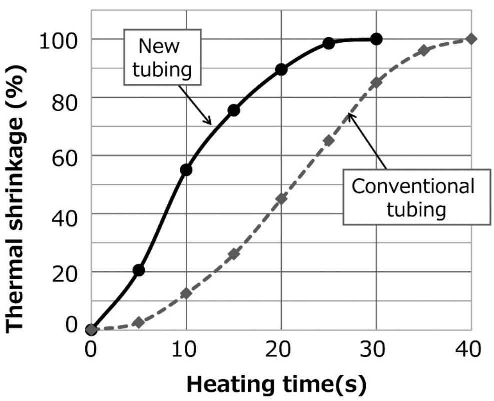


Fig. 8. Evaluation of shrinkage rate (when heated to 110˚C)

5. Conclusions

The authors have developed a very thin-wall, heat-shrinkable tubing using polymer nano-composite technology. With a wall thickness of only 50 μm, the newly developed tubing provides ease of installation comparable to conventional tubing (wall thickness: 200 μm). The new tubing has also been found to have heat characteristics that are comparable to conventional products and the ability to reduce the shrinkage time.

Wide use of the newly developed heat-shrinkable tubing is expected in the fields of electronic devices and components, where the need for thinner wall and lighter weight tubing is increasing.

Technical Terms

*1 Electron beam: A stream of high energy electrons. When a substance is irradiated by the electron beam, the beam's energy is absorbed in the substance causing a chemical reaction such as cross-linking to occur.

*2 Crystalline resin: A polymeric resin that consists of crystalline and amorphous areas. The molecular chains are regularly arranged in crystalline areas, whereas they are randomly distributed an amorphous areas.

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