Dual-Wall Heat-Shrinkable Tubing with Hot-Melt Inner Layer for Anti-Corrosion Protection of Automotive Aluminum Wires

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Heat shrinkable tubing is used for the insulation and mechanical protection of electric wires in fields such as electronics and aircrafts. Among such tubing, dual-wall heat-shrinkable tubing is used for the waterproofing of automotive wiring harnesses at the joints of electric wires. In recent years, with the aim of improving fuel efficiency and reducing vehicle weight for the reduction of CO_2 emissions, aluminum wires have been attracting attention as the replacement of conventional copper wires. We have developed a new dual-wall heat-shrinkable tubing for the anti-corrosion protection of aluminum wires at their terminals.

Keywords: heat-shrinkable tubing, electron beam irradiation, cross-linking, aluminum electric wire, corrosion protection

1. Introduction

Heat-shrinkable tubing, which shrinks radially when heated, is widely used in various industrial fields such as electronics, automobiles, and aircraft for insulation protection of electric wire splices, corrosion protection of piping, and many other purposes. Since 1964, Sumitomo Electric Industries, Ltd. has been producing and supplying heat-shrinkable tubing under the tradename of SUMITUBE. In the 1980s, the company developed dual-wall heat-shrinkable tubing consisting of a hot-melt adhesive inner layer and heat-shrinkable outer layer, and started the production and supply of the tubing. When the tubing is heated for shrinking, the hot-melt adhesive layer melts and conforms to the uneven surface of the object to be covered, thereby exhibiting high insulation protection and waterproofing property. Owing to such distinguishing features, the dual-wall tubing is now used for automobiles, electronics, aircraft, and various other industrial products.

In the field of automobiles in particular, the need to improve fuel efficiency and reduce vehicle weight has recently been growing in response to CO_2 emission regulations. As a means of reducing vehicle weight, the copper conductor of electric wires has been extensively replaced with aluminum conductor. A problem associated with this is how to protect the copper terminal connected to the aluminum conductor from dissimilar-metal corrosion*[1] that occurs at the aluminum/copper joint. This paper reports on the development of new dual-wall tubing that can be used for aluminum electric wires, for which the need to protect terminals from corrosion is growing.

2. Background and Target of the Development

Until now, we have produced and supplied hot-melt adhesive tubing that is mainly useful for waterproofing the wire splices with the single-to-single, single-to-multiple and multiple-to-multiple configurations of PVC*[2]-coated and polyethylene-coated electric wires. Meanwhile, with the spread of the use of aluminum electric wires in automobiles, aluminum wires of various sizes and connectors of various shapes are being designed.[1] A problem associated with large-size, high-current aluminum wires, such as those used as battery cables, is that their anticorrosive treatment is difficult mainly because it takes time to cure the adhesive applied to the connections.

In addition to (1) Preventing elution of aluminum resulting from dissimilar-metal corrosion between the aluminum conductor and copper terminal, attention should be paid to the following two points when covering large size aluminum wires with heat-shrinkable tubing (Fig. 1): (2) Preventing hot-melt adhesive from flowing out of the tubing and entering the bolt fastening hole in the use environment, and (3) Selecting tubing most suitable for the electric wire size and terminal shape to prevent fracturing of the tubing due to stress concentration at the wire edge and/or terminal edge when used.

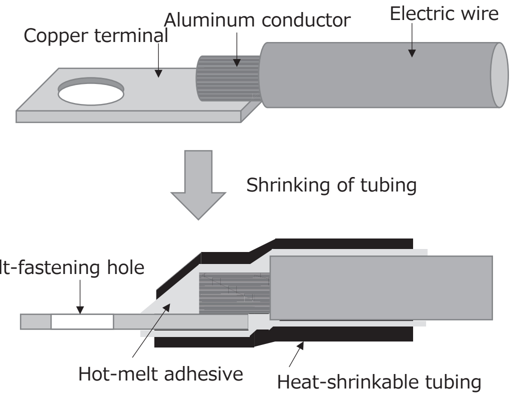

Fig. 1. Schematic illustration of covering terminal-attached aluminum electric wire with heat-shrinkable tubing

Since heat-shrinkable tubing is automatically shrunk on a mass-production basis to enhance work efficiency and eliminate fluctuations in the protection performance of tubing, it is necessary to ensure continuous processability and reproducibility through the use of shrinking machines (Table 1).

Table 1. Differences between newly developed tubing and conventional tubing

	Conventional tubing	Newly developed tubing
Electric wire	Copper wire	Aluminum wire
Configuration	Single-to-single, single-to-multiple, or multiple-to-multiple wire configuration	Dissimilar metal contact between aluminum and copper
Tubing	Maintaining tubing position under use environment	Tear resistance at terminal/wire edge
Adhesive	Conforming of adhesive to the outer surfaces of wire and configuration	Flowability of adhesive not so high as to run into bolt tightening hole
Process condition	Shrinking with shrinking machine on a mass production basis	Shrinking with shrinking machine on a mass production basis

To meet customers' demand for the use of aluminum wires in a temperature environment of -40 to 120°C, the outer layer of the tubing needs to be made of a material that maintains its shape in the use environment and shrinks at a temperature at which the wires do not deteriorate during shrinking. In addition, the adhesive is required to maintain its adhesion of the tubing to the wires and terminals without flowing out of the tubing at 120°C.

Table 2 shows the development target for material selection, and Table 3 shows the target properties of the tubing.

The corrosion protection performance of tubing can be evaluated by checking whether there is a route for an aqueous solution to enter the connection between the aluminum conductor and copper terminal from outside after the connection is covered by the tubing. Subsequent to a durability test, the tubing was subjected to an airtightness test to evaluate its corrosion protection performance by checking its waterproof property.

Table 2. Development target for material selection

		Condition/item	Target
Outer layer	Durability	No cracking after exposure to 1,000 cycles of -40°C for 30 min ⇔ 120°C for 30 min	Tearing strength at 125°C: two times or more that of conventional tubing.
	Processability	Shrinkable by heating not more than 135°C	Heat shrinkable ratio: 70% min.*[3]
Inner layer	Durability	No fluidization of adhesive exposure to 1,000 cycles of -40°C for 30 min ⇔ 120°C for 30 min	No fluidization of overflowed adhesive at 120°C.
	Processability	Adhesion of tubing to conductor, terminal, and electric wire	Waterproofing property in Table 3

Table 3. List of target properties of new tubing

Properties	Item	Target value
Mechanical property	Tensile strength	10.4 MPa min.
	Elongation	300% min.
	Elastic modulus	400 MPa min.
	Heat shock after exposure to 225°C for 4 h	No cracking
	Heat resistance after exposure to 150°C for 168 h	No cracking
Waterproofing property after shrink tubing to the electric wire/terminal	Original property (before durability test)	Air leak test No air leakage from both ends of tubing while pressurization at 200 kPa for 30 s
	Thermal cycle resistance after exposure to 1,000 cycles of -40°C for 30 min ⇔ 120°C for 30 min	
	Salt water resistance after being sprayed with salt water for 96 h	
	Fluid resistance after being immersed in battery fluid for 1 h	
	Oil resistance after being immersed in brake oil for 1 h	

3. Outer Layer of Tubing

3-1 Heat-shrinkable tubing production method and the principle for shrinkage

Heat-shrinkable tubing is produced by three processes: extrusion, electron beam*[4] irradiation, and expansion. A resin is formed into a tube shape in the extrusion process, and the tube is cross-linked in the electron beam irradiation process. In the expansion process, the cross-linked tube is heated and softened, expanded radially by applying internal pressure, and cooled to mold into the shape of heat-shrinkable tubing (Fig. 2). For dual-wall heat-shrinkable tubing having a hot-melt adhesive, a two-layer tube having an adhesive layer added to the inside of the tube is extruded in the extrusion process.

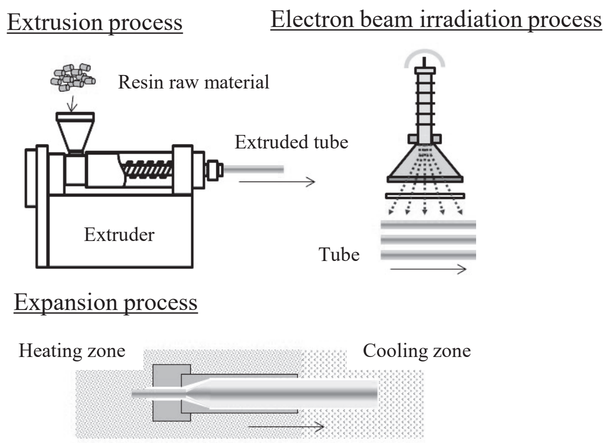

Fig. 2. Heat-shrinkable tubing production process

Figure 3 shows the principle of how tubing develops heat-shrinkability. When a crystalline resin*[5] consisting of both crystalline and amorphous regions is irradiated with an electron beam, the amorphous region forms cross-linking points where the molecules are connected to each other. As a result, the resin becomes a cross-linked resin. The cross-linked resin is expanded by heating and its shape is fixed by cooling to produce an expanded cross-linked resin. When the expanded cross-linked resin is heated to a temperature equal to or higher than the melting point of the crystalline region, the crystal is melted and softened. In this

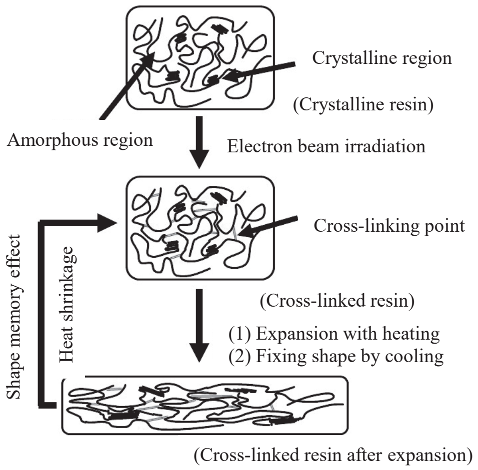

Fig. 3. Principle of heat-shrinkability occurrence

process, the resin causes thermal shrinkage until its shape returns to the shape before expansion because of the presence of the cross-linking points (shape memory effect).(2)

3-2 Development of material

We narrowed down the materials that can be used for the new heat-shrinkable tubing to polyethylene resin after taking into account resistance to hydrophilic battery fluid, resistance to brake oil, possibility of cross-linking by electron beam irradiation, and production cost. As shown in Fig. 4, polyethylene resins having different melting points are commercially available. As density and the number of crystals increase, they enhance the melting point, the coefficient of elasticity, tear strength, and other mechanical properties.

The upper limit of the service temperature is 120°C. Since heat-shrinkable tubing should securely protect electric wires in this temperature range, the melting point of the outer layer material is required to be 125°C or more when a certain allowance is taken into account. Although HDPE*6 is expected to exhibit high strength (piercing, tearing, and so on), its melting point is as high as approximately 130°C. This high melting point may prevent the tubing made of this resin from shrinking to the specified diameter when the tubing is heated to the required temperature of 135°C for one minute.

To develop a material that can shrink to the specified diameter when heated to 135°C, we optimized the melting point of the material by polymer-blending HDPE with various polyethylene materials (Fig. 5).

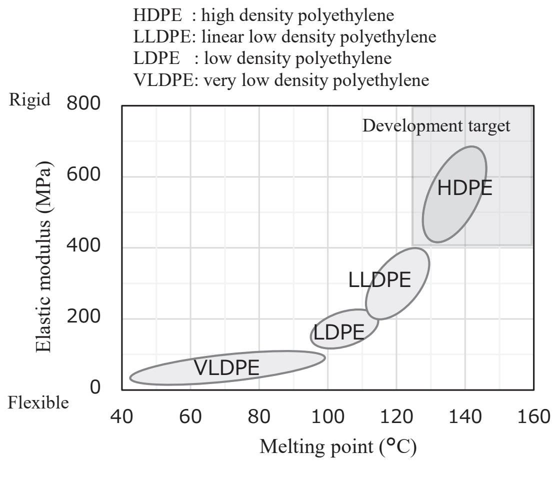

Fig. 4. Dependence of the elastic modulus of various types of polyethylene on melting point

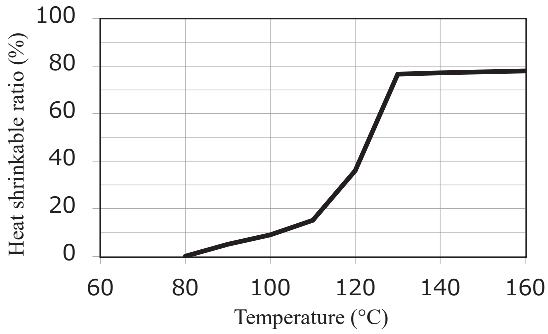

Fig. 5. Temperature dependence of the heat shrinkable ratio

It was also confirmed that the tear strength of the newly developed material at 125°C, which is higher than the service temperature, is 7.6 N/mm. This strength is two times or more that of the conventionally used material.

4. Inner Layer Hot-melt Adhesive

4-1 Polymer alloy

The hot melt adhesive to be used as the inner layers is required to have an adhesive strength that is high enough to adhere to aluminum electric wires, conductors, terminals, and outer layer tubes. A polyamide resin, which has a high degree of design freedom as a hot-melt adhesive, is widely used because of its good adhesion to PVC-coated electric wires. However, this resin does not adhere to polyethylene. To develop an adhesibility between the two resins, we employed polymer alloy technology.

We tested a polymer alloy in which nanometer- to

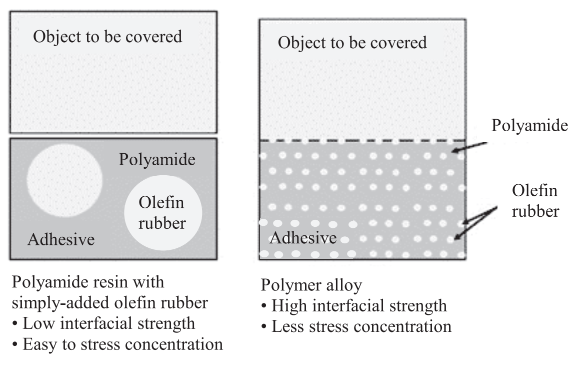

Fig. 6. Difference in adhesion between polymer alloy and polyamide resin with simply-added olefin rubber

micrometer-size olefin rubber were dispersed in a polyamide resin (Fig. 6). The test results verified that the addition of a small amount of olefin rubber is effective to develop a high adhesibility to polyethylene while maintaining high adhesibility to PVC and metals.

4-2 Flowability optimization

To determine the target viscosity of the hot-melt adhesive, we prototyped dual-wall heat-shrinkable tubing using the selected outer layer material and polyamide resins having a different viscosity. A thermal cycle test was carried out in the use temperature range of -40°C to 120°C to check the flowability of the adhesive. As a result, the adhesive exhibited a melt viscosity of 5,000 Pa·s or more at 120°C and did not fluidize at this temperature. Finally, we decided to develop a new dual-wall heat-shrinkable tubing using the inner layer material having the viscosity curve shown in Fig. 7.

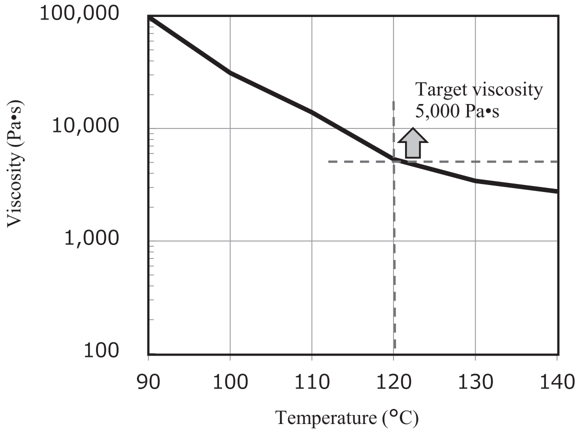

Fig. 7. Temperature dependence of the viscosity of hot-melt adhesive used for new dual-wall heat-shrinkable tubing

5. Evaluation Results for Prototyped Dual-wall Tubing

We prototyped dual-wall tubing (before shrinkage: inner diameter = 17.8 mm; inner layer wall thickness + outer layer wall thickness = 0.8 mm; after shrinkage: inner diameter = 4.5 mm, inner layer wall thickness = 1.4 mm, outer layer wall thickness = 1.0 mm) using the newly developed outer layer material and inner layer hot-melt adhesive. The physical properties and other properties of the prototyped tubing achieved the target values (Table 4).

Figure 8 shows the tubing after exposure to 1,000 thermal cycles. No tearing of the tubing at the edge of the terminal or wire or the flow of the adhesive toward the bolt fastening hole was observed. Thus, the prototyped tubing was found to have maintained the same level of waterproofing properties as that before exposed to the above thermal cycles.

It was also confirmed that the newly developed dual-wall tubing can be continuously shrink-fitted to terminal-attached electric wires by optimally adjusting the shrinking conditions of our belt-conveyer type shrinking machines (Photo 1).

Table 4. Evaluation results for newly developed dual-wall tubing

Properties	Item	Target value	Result
Mechanical property	Tensile strength	10.4 MPa min.	32.1 MPa
	Elongation	300% min.	680%
	Elastic modulus	400 MPa min.	520 MPa
	Heat shock resistance after exposure to 225°C for 4 h	No cracking	Pass
	Heat resistance after exposure to 150°C for 168 h	No cracking	Pass
Electrical property	Dielectric strength	15 kV/mm min.	26.2 kV/mm
	Volume resistivity	10^{12} Ω•cm min.	5.4×10^{16} Ω•cm
Chemical property	Flammability	SAEJ1128 Self extinction of flame within 70 s	Pass
Waterproofing property	Original property (before durability test)	Air leak test No air leakage from both ends of tubing after pressurization at 200 kPa for 30 s	Pass
	Thermal cycle resistance after exposure to 1,000 cycles of -40°C for 30 min ⇔ 120°C for 30 min		Pass
	Salt water resistance after being sprayed with salt water for 96 h		Pass
	Fluid resistance after being immersed in battery fluid for 1 h		Pass
	Oil resistance after being immersed in brake oil for 1 h		Pass

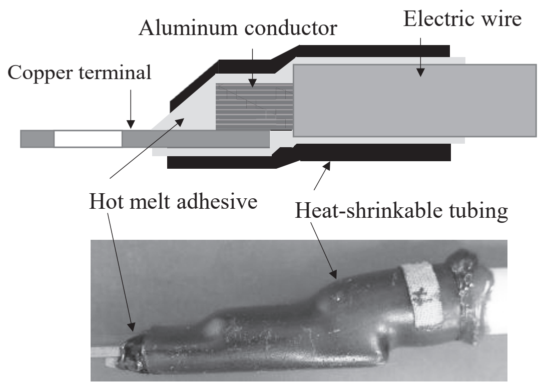

Fig. 8. Tubing after thermal cycle test

Photo 1. Belt-conveyer-type shrinking machine

6. Use for Other Electric Wires

The newly developed dual-wall heat-shrinkable tubing comprising an inner adhesive layer can be used not only for aluminum wires for corrosion protection but also for the waterproofing of PVC-coated and polyethylene-coated wires. Furthermore, there are cases where heat-shrinkable tubing is used for two or more wires fitted with complicatedly shaped terminals. To protect these wires from corrosion and water with heat-shrinkable tubing comprising an inner adhesive layer, it is essential to adhere the tubing to the members surrounding the conductors with no gap when shrinking the tubing and when using the shrink-fitted wires. If it is difficult to fill the gap with the tubing with an adhesive layer alone, the insufficient waterproofing property of the tubing can be compensated for by additionally inserting a supplementary adhesive tube into the conductor or wire when the tubing is shrunk (Photo 2).

Photo 2. Supplementary adhesive tube

7. Conclusions

We have developed dual-wall heat-shrinkable tubing that can be used for corrosion protection of automotive aluminum electric wires. The new tubing has high corrosion resistance to a temperature change from -40°C to 120°C. With the development of autonomous-driving technology, the automotive industry is required to use a greater variety of electric wires than ever. Anticorrosion technology using heat-shrinkable tubing is expected to advance further and will be used more widely in the future.

Technical Terms

*1 Dissimilar-metal corrosion: Also called galvanic corrosion, a phenomenon in which the lower potential one of dissimilar metals in contact corrodes preferentially when an electrically conductive aqueous solution flows between these metals.

*2 PVC: An abbreviation for polyvinyl chloride used for insulation coating of electric wires in a service temperature range of about 80 to 100°C.

*3 Heat shrinkable ratio: A ratio calculated from 100 x (inner diameter before shrinkage - inner diameter after shrinkage) / inner diameter before shrinkage.

*4 Electron beam: A flow of high energy electrons. An electron beam causes a chemical reaction of a substance by colliding with and giving energy to it.

*5 Crystalline resin: A resin containing crystalline regions. Usually, this resin also contains amorphous regions in which molecular chains exist at random.

*6 HDPE: An abbreviation for high density polyethylene, a linear polyethylene with few ethylene chains. HDPE has high crystallinity, high elastic modulus, and high density.

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