ABSTRACT

Because of its outstanding dielectric properties and heat resistance, crosslinked polyethylene (XLPE) is widely used as insulation materials for electric wires and cables. However the three-dimensional lattice structure produced by crosslinking makes it impossible to melt it down again for molding. Thus almost all waste XLPE is currently burnt (as a fuel) or disposed of in landfills. In this work the authors have developed technology in which the application of suitable heating and shearing to XLPE decreases its molecular weight, producing a recycled material that is sufficiently thermoplastic to allow it to be molded, and have evaluated the physical properties of the recycled material obtained. The crosslinked content remaining in the recycled material is from about 1 to 40 %; the melt flow rate (MFR) is in the range of 0.1 to 30 g/10 min, and the chemical structure is substantially the same as the original material, making it possible to recycle it to various applications using ordinary molding equipment.

1. INTRODUCTION

As part of Furukawa Electric’s wide-ranging environment protection activities, we are actively participating in material recycling programs aimed at the reduction of industrial waste and the reuse of waste materials, to develop comprehensive recycling technologies and systems, and achieve an environment-friendly society. Among Furukawa Electric’s many product lines, electric wire and cable is one in which recycling systems are comparatively well established, but while recycling rates for the copper and aluminum used as conductors are something like 99 %, the amount of sheathing material that is recycled is very low.

It is true that for some sheathing materials--the PVC widely used for electric power cable sheathing and telecommunications cables as well as the polyethylene used for telecommunications cables--a considerable proportion is made into pellets and reused. For other sheathing materials, most particularly XLPE, on the other hand, almost all but that portion that is thermally recycled by use as auxiliary fuel is disposed of as industrial waste in landfills. It is estimated that the amount involved in Japan is about 10,000 tonnes per year. This is because there is no effective material recycling technology to handle XLPE, and no hope that effective industrial-scale recycling can be implemented. In the present work an attempt has been made to use thermoplasticizing technology to recycle the peroxide crosslinked and silane crosslinked polyethylenes commonly used as the insulation of electric wires and cables, and a report is made on the various properties of the recycled materials obtained and the results of analysis.

2. RECYCLING OF XLPE

Crosslinked polyethylene, which is in wide use mainly as insulation for electric wires and cables, is a material in which the polyethylene molecule chains have been crosslinked by such means as organic peroxides, ionizing radiation or silane compounds. Because of the formation of a gigantic three-dimensional lattice structure it becomes heat resistant, holding its shape even when heated above its melting point. It is thus an extremely useful material that has superior dielectric properties, but unlike ordinary thermoplastic materials it has the disadvantage that it cannot be melted down and molded for recycling. Thus like rubber and thermosetting plastics, it is virtually impossible to reuse XLPE in the same application.

Techniques that have been used in the past to recycle XLPE include conversion by pyrolysis into oils or waxes, and pulverization for use as fuel or filling material. Recently much work has been done on developing recycling technology using supercritical fluids and it has been reported that thermoplasticizing through selective cracking of the crosslinked structure has yielded high-quality recycled materials, but it seems that problems persist, relating to the cost of equipment and the feasibility of continu-
ous processing. There have also been reports of technology for adding thermoplastics to the waste XLPE and melting the mixture to obtain recycled material that is thermoplasticized.4,5)

The work reported here has been supported by the Enterprise for Assisting in the Development and Implementation of Industrial Technologies of NEDO, the New Energy and Industrial Technology Development Organization, and constitutes a technology for obtaining a thermoplastic recycled material by breaking down the crosslinked structure of XLPE through the use of appropriate heat and shearing. Since the recycled material can be melted down and molded in the same way as ordinary thermoplastic materials it has the advantage that it can be reused without additional material.

3. RECYCLING BY THERMOPLASTICIZING

The process for obtaining a thermoplastic recycled material by breaking down the crosslinked structure of XLPE and reducing the molecular weight is referred to as thermoplasticizing. Figure 1 diagrams the process.

Since the recycled material obtained does not have the three-dimensional lattice structure of XLPE, it is transformed into a thermoplastic material that can be melted when heated above the melting point that polyethylene had before it was crosslinked.

Figure 2 is a flow chart of the thermoplasticizing process for obtaining recycled material using the XLPE waste from electric wires and cables as the raw material. XLPE waste is removed from electric wires and cables and processed into nuggets preparatory to be discharged. It may then, if required, be separated or sorted, and be cleaned or have foreign matter removed. It is then broken down into particles of a size suitable for feeding into the processing equipment. The XLPE chips are then loaded into the feeder unit, and supplied continuously in measured amounts to the thermoplasticizing equipment. By making appropriate adjustments to the structure of the thermoplasticizing equipment and the processing conditions it is possible to make from the XLPE a material of lower molecular weight. The thermoplastic material discharged from the equipment is then cooled and made into pellets.

4. EXPERIMENTS

4.1 Raw Material

It would be desirable to use the XLPE waste recovered from wires and cables in actual service, but since it is difficult to determine the history of the materials arising from differences in usage environments, two XLPEs equivalent to those used in wires and cables were manufactured for use as the raw materials. These were:

- XLPE-a (peroxide crosslinked polyethylene):
  a low-density polyethylene made by crosslinking using organic peroxide compounds, with a degree of crosslinking (gel content) of approximately 80%;

- XLPE-b (silane crosslinked polyethylene):
  a linear low-density polyethylene made by crosslinking using silane, with a degree of crosslinking (gel content) of approximately 60%.

4.2 Pre-processing and Thermoplasticizing

The raw materials were processed in a single-axis rotary blade chipping machine into chips approximately 5 to 10 mm square. Photo 1 shows the material before processing and the chips. No washing or cleaning, or processing to remove foreign matter was performed.

The XLPE chips were then fed to the thermoplasticizing equipment, where they were converted under differing process conditions into pellets of recycled material measuring 2 to 3 mm in diameter by about 3 mm.

![Figure 1](image1.png)

**Figure 1** Outline of the process of thermoplasticizing crosslinked polyethylene.

![Figure 2](image2.png)

**Figure 2** Flow chart of thermoplasticizing process for recycling of XLPE waste from electric wires and cables.
4.3 Evaluating Properties of Recycled Material

4.3.1 Sample Materials
Two recycled materials—XLPE-a and XLPE-b which had been thermoplasticized from two types of XLPE were used, together with low-density polyethylene (LDPE), having a density of 0.92 g/cm³ and an MFR of 1.0 g/10 min, as a control.

4.3.2 Observation
Surface condition and coloration, transparency, etc. were observed visually.

4.3.3 Melt Flow Rate
In accordance with JIS K7210, the MFR was measured at a test temperature of 190°C and a test load of 21.8 N.

4.3.4 Degree of Crosslinking (gel content)
A sample of approximately 0.1 g (w₁) was wrapped in 400-mesh stainless steel mesh of known mass (w₂) and exposed in 100 ml of xylene at 120°C for 24 hr. The stainless steel mesh was then removed and the mass measured after vacuum drying at 80°C for 16 hr (w₃). The degree of crosslinking was measured in terms of the percent gel content, using the equation

\[ \text{gel content (\%)} = \left( \frac{w_3 - w_2}{w_1} \right) \times 100 \]  

(1)

4.3.5 Melting Point
Measurements of the melting point were made by differential scanning calorimetry (DSC) at a temperature rise rate of 10°C/min and of the quantity of heat to melting. The peak top temperature of the heat absorption peak was taken as the melting temperature.

4.4 Evaluating Molding Properties

4.4.1 Press Molding
After being mixed by an open roll, the recycled material was formed on a hot press into sheets 1 mm in thickness, and its flow properties and the condition of the sheet surface were checked.

4.4.2 Extrusion Molding
Sheet extrusion was carried out using a 40 mm diameter single screw extruder with a cylinder temperature of 160°C and a die temperature of 180°C. The extruded sheets were taken up onto a cold roll yielding sheets approximately 2.0 mm in thickness.

4.5 Analysis

4.5.1 Sample Materials
We used representative samples of recycled materials and LDPE as a control.

4.5.2 Infrared Absorption Spectrum
The infrared absorption spectra of samples made by the hot pressed film method were measured using FT-IR.

4.5.3 Molecular Weight Distribution
The molecular weight distribution in the samples was measured by gel permeation chromatography (GPC). We used ortho-dichlorobenzene as the solvent, a Shodex AD-806MS GPC system, a measuring temperature of 140°C, and an infrared spectrophotometer as the detector. Molecular weight was calculated by universal calibration using a standard PS.

4.5.4 Short-Chain Branches
Short-chain branches were analyzed by measuring the 13C-NMR (nuclear magnetic resonance) spectrum. The chip samples were first processed in a Soxhlet extractor using acetone and then dissolved by heating to 120°C in a mixed solvent of ortho-dichlorobenzene and deuterated benzene.

5. EXPERIMENTAL RESULTS AND DISCUSSION

5.1 Evaluation of Properties
Photo 2 shows pellets of recycled XLPE-a, and Table 1 shows the results of evaluating the materials tested. The pellets of recycled material were pale brown to pale gray, and both the recycled materials were more discolored than, and somewhat inferior in transparency to, the LDPE used as a control. With respect to the surface, the XLPE-a was smooth, but the XLPE-b was somewhat rough.
There was a broad range of MFR for the recycled materials produced under various conditions, from 0.1 to 30 g/min. The gel content, which indicates the degree of crosslinking, dropped to about 1% in most of the recycled XLPE-a material, and the reduction in molecular weight proceeded until there was virtually no gel content. In XLPE-b, by contrast, there was a residual gel content of about 30%, but most of the unmelted gel in the XLPE-b was in the form of particles smaller than 1 mm, not a type of gel content that would retain the configuration of the sample. Measurements of MFR for the recycled XLPE-b also showed adequate flow properties, so that, despite the fact that the macro crosslinked structures were largely broken down, it seems not to have reached the point of complete reduction in molecular weight.

Figure 3 is a chart showing the results of DSC for the recycled XLPE-a and XLPE-b, and the LDPE control material. Both of the recycled materials were seen to exhibit a clearly defined melting point, and it was confirmed that the quantity of heat absorbed was not significantly different from the ordinary LDPE.

5.2 Molding Properties
Both in press molding and extrusion molding the recycled materials exhibited exactly the same molding properties as the LDPE used as a control. In extrusion molding, there were some difference in flow properties due to the different MFRs but there was no increase or fluctuation in extrusion torque, and the surface properties were satisfactory for both materials. These results confirmed that the recycled materials have satisfactory molding properties.

5.3 Results of Analysis
Figure 4 shows the FT-IR absorption spectra of the recycled XLPE materials and the LDPE used as a control. XLPE-a showed virtually identical results to the LDPE, but XLPE-b exhibited absorption due to silane crosslinking. This was virtually the same as the absorption spectra of the XLPE raw material, showing that there were virtually no chemical changes, with the exception of the reduction in molecular weight due to the thermoplasticizing processing. Among the points of difference was a slight increase in absorption at about 900 cm\(^{-1}\) for the recycled materials due to the vinyl group and the vinylidene group, suggesting that there was a slight increase in the C=C double bond due to thermoplasticizing.

Table 2 and Figure 5 show the results of measurements of the molecular weights of the two recycled XLPE compounds and the LDPE used as a control. It can be seen that while the weight-average molecular weight was about 30,000 for the LDPE versus about 100,000 for XLPE-a, the peak top molecular weight was, in contrast, lower for the recycled materials. This is due to the comparatively large amount of constituents having molecular weights greater than 100,000 that remained in the recycled materials.
The mechanism of this reaction is similar to the random heating and shearing, and it is assumed that the reaction progresses as the XLPE raw material is subjected to appropriate equipment, a molecular weight reducing reaction process. In the thermoplasticizing of XLPE can be controlled to a level approaching that of polyethylene before crosslinking. In the thermoplasticizing process, the level of molecular weight reduction by optimizing the configuration and operating conditions of various equipment, the level of molecular weight reduction during thermoplasticizing appeared as a result of differences in the methods of crosslinking. It is necessary to note, however, that for recycled XLPE-b, the molecular weight of the approximately 30% gel content remaining was not included in the measurement results.

Analysis of short-chain branch structures by \textsuperscript{13}C-NMR showed that they were virtually the same in the LDPE control and XLPE-a recycled material, whereas the XLPE-b recycled material had a structure with relatively more ethyl branches. This is primarily due to the polyethylene material prior to crosslinking, making it possible to confirm that there was virtually no change in short-chain branch structure due to thermoplasticizing. Also, C=C double bonds were detected, though in miniscule quantities, from the recycled material, results that were congruent with the infrared absorption spectra.

### 5.4 Mechanism of Thermoplasticizing Process

The results of our evaluations and analyses told us that the recycled materials made from XLPE by a process of thermoplasticizing showed differences from virgin polyethylene in that they had a certain amount of minute crosslinking and residual constituents of somewhat high molecular weight, and that double bonds formed with the reactions reducing molecular weight, to which discoloration may be attributed. From the chemical standpoint, however, it can still be called polyethylene.

The technology developed here is characterized in that, by optimizing the configuration and operating conditions of various equipment, the level of molecular weight reduction of XLPE can be controlled to a level approaching that of polyethylene before crosslinking. In the thermoplasticizing equipment, a molecular weight reducing reaction proceeds as the XLPE raw material is subjected to appropriate heating and shearing, and it is assumed that the mechanism of this reaction is similar to the random decomposition that occurs in the thermal cracking of ordinary XLPE.

Furthermore it has been found that polyethylene crosslinked by organic peroxides yields a satisfactory recycled material of good appearance and little residual gel content. In contrast, when the raw material was polyethylene crosslinked by silane, the recycled material had a somewhat rough surface and even when MFR was comparatively high, a crosslinked component remained. It is thought that this is because when silane XLPE is subjected to molecular weight reduction, the polyethylene chains are severed preferentially, while the siloxane bonds of the crosslinks are not severed.

### 5.5 Suitability of Materials to Recycling

By a thermoplasticizing process of XLPE, it is possible to obtain a recycled material having virtually the same molding properties and molecular structure as polyethylene. With the exception of the preparation and chipping of the raw material, this process is simple and continuous, with a yield approaching 100%. Productivity is comparatively high, and depending on the scale of the equipment, outputs of several tonnes of recycled material per day are possible.

Although the results of this work are based on studies of the use of virgin XLPE, it was possible to use the recycled material by itself in molding. Thus it can be used in a wide range of material recycling applications, including reuse as sheathing for electric wires and cables.

When, however, it is desired to recycle XLPE waste salvaged from wires and cables that have been in use, it is necessary to consider the deterioration caused by the conditions of use, the adherence of foreign matter, and the admixture of materials other than XLPE during the stripping process. Since sheathing materials for electric wires and cables must be superior in appearance, mechanical properties, electrical properties and durability, we feel that in establishing closed-loop material recycling, consideration must be given to salvage systems and technologies for reuse.

### 6. CONCLUSION

It has been confirmed that through the technology of thermoplasticizing for recycling that has been developed in this work, it has been possible to obtain from crosslinked polyethylene a recycled material, the molecular weight of which is sufficiently reduced to allow it to be reused. The following conclusions have been reached:

1. Both peroxide-crosslinked and silane-crosslinked polyethylenes can be thermoplasticized, and the recycled materials have gel contents of about 1~40% and MFRs in the range of 0.1~30 g/10 min. The recycled material from peroxide-crosslinked polyethylene is superior to that from silane-crosslinked polyethylene in terms of better appearance and lower residual gel content.

2. The recycled materials can be press-molded and
extrusion molded without additional material.

(3) The chemical composition of the recycled materials is substantially the same as that of polyethylene, with some slight increase in double-bond component. There are also residual components with molecular weights greater than 100,000. These results confirm that thermoplasticizing recycling technology enables crosslinked polyethylene to be reused. The technology presented here is highly feasible from the standpoints of productivity and cost, and seems to be an effective method of reducing environmental impact by reusing the crosslinked polyethylene waste that has in the past been used as fuel or disposed of as industrial waste.

REFERENCES


