Return to Session

DEVELOPMENT OF RECYCLING TECHNOLOGY OF XLPE

Yoitsu SEKIGUCHI, J-Power Systems Corp., (Japan), sekiguchi.youitsu@jpowers.co.jp
Noriyuki OHKAWA, J- Power Systems Corp., (Japan), ohkawa.noriyuki@jpowers.co.jp
Hitoshi NOJO, J- Power Systems Corp., (Japan), nojo.hitoshi@jpowers.co.jp
Satoru HASHIMOTO, J- Power Systems Corp., (Japan), hashimoto.satoru@jpowers.co.jp

ABSTRACT

Recently, to reduce environmental damage, various studies on recycling technologies of various materials have been examined. Those of poly-ethylene and PVC are well-known within the construction materials of wires and cables, while that of cross-linked polyethylene (XLPE) has not yet been done, since it is very difficult to be thermo-plasticized because of its chemical cross-linking structure. We have studied solid-state grinding by mill and thermo-plasticization by twin-screw extruder as recycling treatments. Prototype insulation wires using the recycled materials were manufactured by production machine and evaluated. The results show that they work well as insulation wire.

KEYWORDS

XLPE, Recycling technology, Thermo-plasticization

1. INTRODUCTION

Recently, as it has become more and more important to reduce environmental damage, various studies on recycling technologies of cable construction materials have been examined. Up to now, efficiently recycling metallic materials as valuable resources by collecting wire and cable scraps and techniques to separate metallic materials from others have been well developed in Japan, while a recycling method of XLPE was less studied[1].

XLPE is an excellent material as insulation for wires and cables, but very difficult to be thermo-plasticized because of its chemical cross-linking structure. Therefore, most XLPE waste has been thrown away or thermally recycled as fuel. For material recycling of XLPE waste, we are studying solid-state grinding by mill and thermo-plasticization by twin-screw extruder as recycling methods[3][4].

2. ABOUT XLPE

As detailed below, the difference between two types of cross-linking bonds causes different results of thermo-plasticization by the molten state shearing method. The variety of XLPE should first be described.

Chemical structure of XLPE

XLPE is commonly applied as insulation for wires and cables, in which two types of cross-linked polyethylene are used. One is peroxide XLPE, the other is silane XLPE.

(1) Peroxide XLPE

Additives such as antioxidant and peroxide, and polyethylene is first compounded, then the compound is extruded as wire or cable and heated in a continuous vulcanizer such as CCV and VCV. By heating, peroxides generate alkyl-oxy radicals which act as initiators of cross-linking reactions. Electrons are transposed from alkyl-oxy radical to polyethylene chains, then form radicals on molecular chains of polyethylene. Two radicals on polyethylene form a new carbon-carbon bond which acts as cross-linking. (See Fig.1 (a)) Peroxide XLPE is abbreviated to 'P-XLPE'.

(2) Silane XLPE

Silane coupling agents are first graft polimerized to molecular chains of polyethylene, then silane grafted polyethylene is extruded as wire or cable. Instead of heating, a catalyst induces cross-linking between two silane coupling agents. (See Fig.1 (b)) Silane XLPE is abbreviated to 'S-XLPE'.

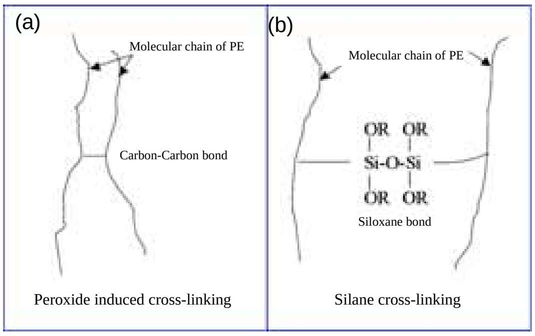


Figure 1: Types of cross-linking of XLPE

3. RECYCLING METHODS OF XLPE

Fig.2 shows the flow of recycling of wires and cables. To collect copper and aluminium as valuable materials, collection routes and methods are well developed, then XLPE waste is also collected using the same route. We have been studying (1) a solid-state shearing method, and (2) a molten state shearing method, as recycling methods for XLPE.

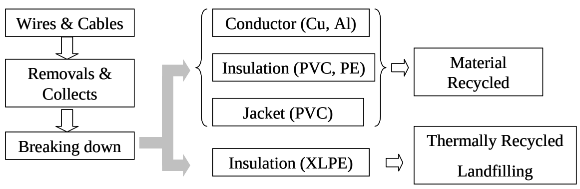


Figure 2: Recycle flow of wire and cable

Table 1: Properties of the recycled materials

	S-XLPE	Solid state shearing method	Molten state shearing method		Raw material (LDPE)
			Condition (A)	Condition (B)	
MFR (g/10min)	Impossible	Impossible	20	0.1	1.3
Gel fraction (%)	65	52	0	42	0
Tensile strength (MPa)	20.9	Impossible	10.2	9.6	22
Elongation (%)	510	Impossible	70	180	760

- Condition (A) of molten state shearing method refers to the condition at higher shearing rate, and condition (B) refers to the condition at lower shearing rate.
- MFR: Radius of orifice is 2.0mm, with a weight of 2.16kg at 190^{o}C.
- Gel fraction: in hot xylene at 110^{o}C for 24h
- Tensile test: at room temperature, tensile rate 200mm/min

(1) Solid state shearing method

In the solid state shearing method, XLPE is treated by a mill at room temperature.

The S-XLPE insulation layer of overhead distribution wires (OC wire) were used as the XLPE waste. The insulation layer of OC wire was removed first, and then chipped into small pieces of 5-10mm by a grinding machine. The chipped XLPE waste is further ground by a mill into a fine powder of approximately 0.3mm.

(2) Molten state shearing method

To develop the molten state shearing method, we studied some kneading machines to add shear to XLPE waste at high temperatures beyond the melting point of polyethylene. As a result of our examination, a twin-screw extruder was found to be the most effective to thermo-plasticize XLPE waste. The chipped XLPE waste was treated with a twin-screw extruder at high temperatures beyond 200^{o}C.

The difference between the materials recycled by the solid state shearing method and by the molten state shearing method is shown in Fig.3.

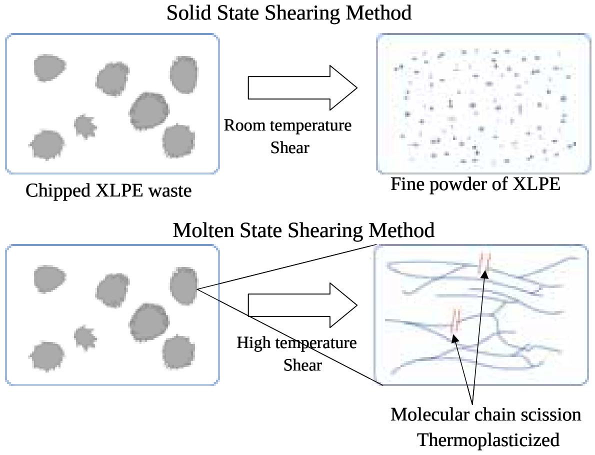


Fig.3 Difference between the material recycled by the solid state shearing method and by the molten state shearing method

4. PROPERTIES OF RECYCLED MATERIALS

The properties of the recycled materials which were treated by the methods mentioned in Clause 3 are described in this Clause.

Using S-XLPE of OC wire, recycled materials were obtained by the solid state shearing method and the molten state shearing method. Recycled materials mixed and unmixed with new polyethylene were evaluated.

4-1. Unmixed materials

The melt flow rate (MFR), gel fraction, tensile strength and elongation were evaluated.

(1) Melt flow rate

The Melt flow rate (MFR) was measured with a weight of 2.16kg at 190^{o}C. Since the recycled materials obtained by the solid state shearing method still have a chemical structure of XLPE, they could not be melted, and it was impossible to measure MFR. On the other hand, since the recycled materials obtained by the molten state shearing method were thermo-plasticized, the MFR could be measured.

(2) Gel fraction

Gel fraction was measured as remains of recycled materials except for dissolving fraction in xylene at 110^{o}C. Since the recycled materials obtained by the solid state shearing method still have a chemical structure of XLPE, they could not be dissolved in xylene, gel fraction was still at a high level.

(3) Tensile test

Mechanical properties were evaluated by the tensile test. Since the recycled materials obtained by the solid state shearing method could not be applied to sheet samples, it was impossible to measure their properties. The recycled materials obtained by the molten state shearing method could be applied to sheet samples by press molding. Using a dumbbell specimen cut from the pressed sheet, a tensile test could be made. Properties could be varied according to the condition of thermo-plasticization, strength and elongation of the recycled materials were not suitable for use. (See Table 1)

4-2. Influence of chemical structure of XLPE

As described in Clause 2, two types of XLPE have been applied to the insulation layer of wires and cables. S-XLPE was evaluated in the previous clause, the difference between S-XLPE and P-XLPE is discussed in this clause.

Table 2: Bond energy of single bond in XLPE [2]

	Bond energy (kJ/mol)
C-C	348
C-H	413
Si-O	369
C-Si	290

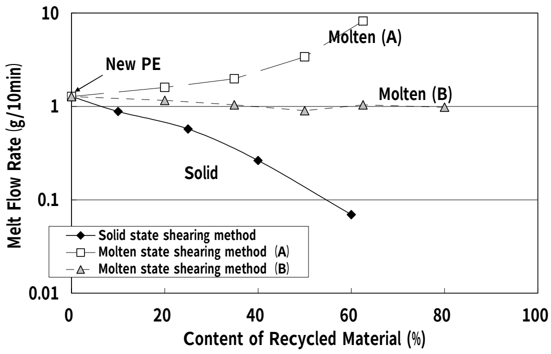


Fig.4: The effect of content of recycled materials to MFR

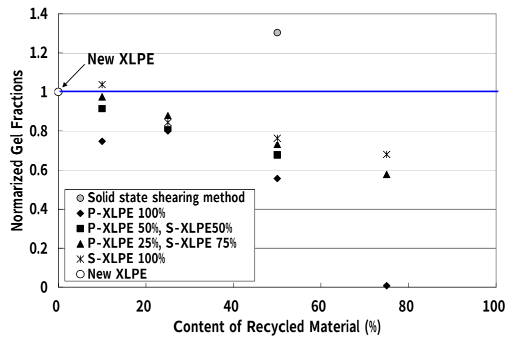


Fig.5: The effect of content of recycled materials to gel fraction

Table 2 shows the bond energy of individual single bonds which commonly exists in XLPE. The bond energy of Si-O is stronger than those of C-C and C-Si, so it is expected that the siloxane bond will be tougher than C-C or C-Si bond.

To compare the two types of XLPE, varying the mixing ratio of two XLPE, treatment of XLPE by a twin-screw extruder was undertaken. From the evaluation of MFR, gel fraction and tensile test, it can be seemed that thermo-plasticization is more advanced in P-XLPE than in S-XLPE.

4-3. Mixed with new polyethylene

In the previous clause, it turned out that thermo-plasticized material by twin-screw extruder did not have enough properties as an insulation of wire and cable by itself. To improve the properties of recycled materials, an addition of new polyethylene was considered.

(1) Melt flow rate

Fig.4 shows the effects of the content of recycled materials to the MFR. In the case of materials obtained by the solid state shearing method, MFR decreases rapidly as the content of recycled material is increased. On the other hand, in the case of material obtained by the molten state shearing method, depending on the MFR of recycled materials by themselves, MFR of mixed materials are controllable.

(2) Gel fraction after cross-linking

After cross-linking of recycled materials which was mixed with new polyethylene, gel fraction was measured. Fig.5 shows the relationship between the content of recycled materials and gel fraction. Gel fraction was normalized so that the value of new XLPE became “1”. According to the increase of content of recycled materials, gel fraction tends to decrease, especially in the case of P-XLPE. As thermo-plasticization is more advanced in P-XLPE than in S-XLPE, it was considered that recycled P-XLPE contained lower molecular weight segments which made cross-linking of XLPE more difficult.

(3) Tensile test

Using the same samples as measuring MFR, the tensile test was evaluated. Fig.6 shows the relationship between the content of the recycled materials and elongation before cross-linking. According to the increase of content of recycled materials, elongation tends to decrease. In the case of the molten state shearing method, the decrease of (A) starts from lower content of the recycled

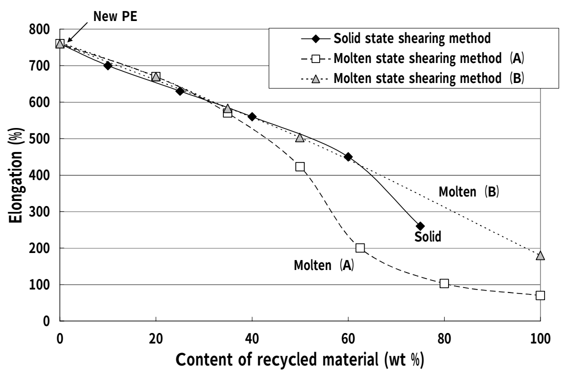
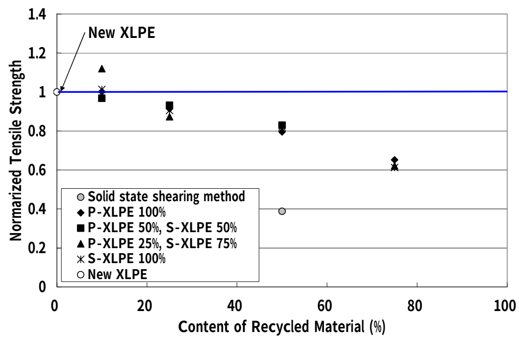
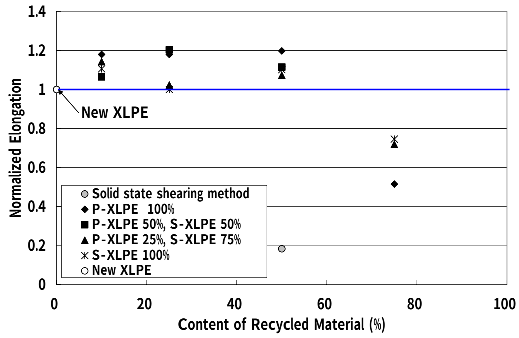


Fig.6: The effect of content of recycled materials to elongation (before cross-linking)



(a) Tensile strength



(b) Elongation

Fig.7: The effect of content of recycled materials to tensile test results (after cross-linking)

materials than that of (B).

Also, using the same samples as measuring gel fraction, the tensile test was evaluated. Fig.7 shows the relationship between the content of recycled materials and tensile strength (a) and elongation (b) after cross-linking. The values of vertical axes were normalized so that the values of new XLPE became "1". In the case of the solid state shearing method, when the content of recycled material was 50%, the normalized strength went down to 0.4 and the normalized elongation to 0.2. In the case of the molten state shearing method, a decrease of elongation was not found up to 50% of recycled materials and a gradual decrease of strength was found. It turns out that the elongation was improved by cross-linking. At the point of 50% content of recycled materials, as the normalized strength shows above 0.8, there is almost no problem from a practical view point.

In conclusion, recycled materials obtained by the molten state shearing method have difficulties in the mechanical properties when used alone, but they could be used by mixing with new polyethylene. When the lower limit of characteristic fall was estimated at 80%, the available upper limit of content of recycled material would be 25-30%.

5. EVALUATION OF PROTOTYPE WIRES

Prototype wires using recycled materials were manufactured and evaluated.

5-1. Experimental trial

Using a mix of recycled material and new polyethylene, prototype insulation wire was manufactured by experimental machine. The dimensions of the prototype wires were 5.5mm^2 of conductor and 3mm of insulation thickness. Monosyl type processing in which compounding and extrusion were simultaneously processed was applied. The recycled material percentage and evaluation results are written in Table 3. In the case of the solid state shearing method, the surface appearance was not good so that its ability to withstand

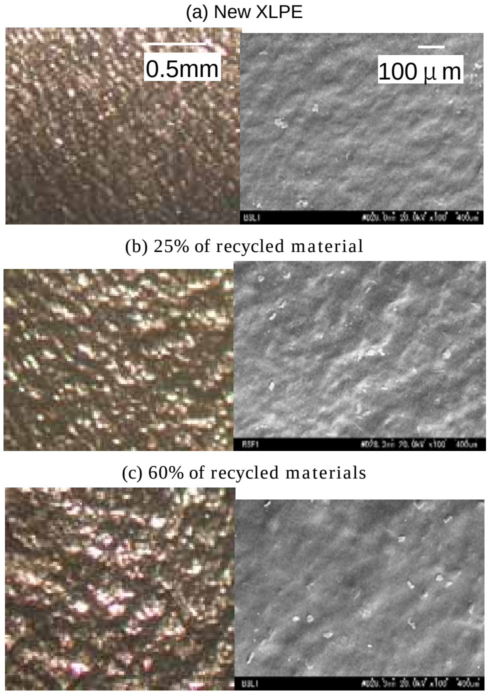


Fig. 8: Microscopic and SEM images of prototype wires made by recycled materials

Table 3: Properties of model wire made using the recycled materials

No.	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5
Method	Molten A	Molten B		Solid	New
Content of recycled materials (%)	25	25	50	50	0
Withstand voltage test (1)	Good	Good	Good	Good	Good
Tracking resistance (2)	Good	Good	Good	No good (1/3)	Good
Surface appearance	Smooth – slightly rough	Smooth – slightly rough	Slightly rough	Rough	Smooth

(1) Withstand voltage test: 12kV 1min

(2) Tracking resistance: Based on JIS C 3005 4.13. After 101 times sprays of test solution when 4kV is applied, leakage current shall be under 0.5A and it shall not be burned.

Table 4: The influence of the content of recycled materials to the properties of model wires

Items			Specification	Content of recycled materials (%)				
				0	25	40	60	75
Withstand tracking test (1)				Good	Good	Good	Good	Good
Tensile test (2)	at RT	Tensile strength (MPa)	>10MPa	15.6	15.8	13.9	12.4	13.1
		Elongation (%)	>350%	407	410	417	407	440
	Aged	Rate of strength (%)	>80%	100.8	102.5	112.7	129.8	109.2
		Rate of elongation (%)	>80%	91.7	96.8	99.1	104.9	94.8
AC break down test (kV)			—	55	70	50	50	50

(1) Tracking resistance: Based on JIS C 3005 4.13. After 101 times sprays of test solution when 4kV is applied, leakage current shall be under 0.5A and the sample shall not be burned.

(2) Tensile test: Rate of pulling is 200mm/min. Aging condition is at 120^{o}C 96h.

Return to Session

tracking test was worse than in the case of the molten state shearing method. In the case of the molten state shearing method, the surface appearance became worse than new XLPE, but the properties of the trial wires were almost the same as new wire.
The influence of the content of recycled materials to prototype wires is shown in Table 4. Thermo-plasticized materials by the molten state shearing method were applied to this trial manufacturing. Though the content of recycled materials increased up to 75%, characteristic fall was not found because an improved material was used. Microscope images and SEM images are shown in Fig.8. Although the surface becomes rougher with an increase of recycled materials, it has not yet led to electrical defects.

5-2. Trial by production machine

From the results mentioned above, a trial production of wires by production machine was carried out at 25% of recycled materials. The specifications of the prototype wire are shown in Table 5.

Table 5:Configuration of the prototype wire by the production machine

Items	Configuration
Conductor	Al
Size	$240mm^2$
Thickness of insulation	3mm

Monosyl type processing in which compounding and extrusion were simultaneously processed was applied as well as prototype wire by experimental machine.
To make the difference between the type of XLPE clear, 3 kinds of materials, those of 100% of S-XLPE, 50% of S-XLPE and 50% of P-XLPE, and 100% of P-XLPE were used. And the content of recycled materials was 25% in all cases. Evaluation results are shown in Table 6 and photograph of prototype wire using the recycled material from 100% of S-XLPE is shown in Fig.9. The properties of the prototype wires were quite good for all three types.

5-3. Characteristic concern in long-term usage of recycled materials and its evaluation

We have been developing insulation wire using recycled materials which has a performance equal to new

Fig.9 Photograph of the prototype wire using the recycled material

insulation wire, it should be noted that there are risks in using recycled material especially in long term usage. Items of concern and their evaluation results are described in this clause.

(1) Influences of repeated recycling

When recycled wires and cables come to be used widely, it can be easily imagined that the recycled wires and cables will mix with the scrap. Recycling by the molten state shearing method was carried out repeatedly, then manufactured wire using the recycled material was evaluated.
Using XLPE waste from scrap wire, a first recycling treatment was done. After the second recycling, previous prototype wire was used as a source of XLPE waste.
As a result, characteristic fall was not found even after 5 repetitions.

(2) Weather resistance

The weather resistance of the prototype wires were estimated.
To create the weather resistance, a small amount of carbon black is blended in the insulation of OC wires. As carbon black was already blended in scrap wire, it will be a problem to control the amount of carbon black in the insulation.
Accelerated test by exposure to light of the carbon arc was carried out covering the prototype wires. The oxidation state of the surface, presence of cracks, and

Table 6: Evaluation results of the prototype wires

	Trial A	Trial B	Trial C	New wire
Type of XLPE	S-XLPE 100	P-XLPE 100	S-XLPE 50／P-XLPE 50	—
Content of recycled materials (%)	25	25	25	—
Withstand voltage test (1)	Good	Good	Good	Good
Tracking resistance (2)	Good	Good	Good	Good
Surface appearance	Good	Good	Good	Good
Heat deformation (3)	31	36	34	17-34

(1) Withstand voltage test : 12kV 1min
(2) Withstand tracking test : After 101 times sprays of test solution when 4kV is applied, leakage current shall be under 0.5A and the sample shall not be burned.
(3) Heat deformation At the conditions of load 39.2N, temperature 120°C, pre-heating 30min, pressing 30min. Distortion ratio shall be lower than 40%.

tensile test were evaluated. As a result, a significant fall of properties was not found.

(3) Environmental stress cracking test

ESCR was estimated by using the samples from prototype wires trial A, B, C and a 5th repetition of recycling. All samples showed good performance (no cracks up to 2000h) equal to new insulation wire.

6. CONCLUSION

(1) The solid state shearing method and the molten state shearing method were examined. A mill was applied as the solid state shearing method, it was found that XLPE could be ground to 0.3mm of fine powder. A twin screw extruder was applied as the molten state shearing method, it was found that XLPE could be thermo-plasticized under adequate conditions.

(2) Using the recycled material mentioned in (1), prototype insulation wires were manufactured and evaluated. Recycled materials by the molten state shearing method were found to be of practical use as insulation for wires.

Acknowledgments

We would like to thank the staff from the Distribution Department in the Distribution Management Group of Tokyo Electric Power Company for their instructive advice about the study.

REFERENCES

[1] Sachio Tazawa, 2003, "*Recycling of Insulated Wire and Cable and Technologies for Low Environmental Impact*", IEEJ.Trans.PE, Vol.123-B, No.3, 265-268.

[2] L. Pauling, 1960, *Nature of the chemical bond 3rd ed.,* Cornell University Press, Ithaca, USA.

[3] Yoitsu Sekiguchi, Hitoshi Nojo, Noriyuki Ohkawa, 2006, "*A Study on Recycling Technology of Cross-Linked Poly-Ethylene*", Proc.17th Annual Conf. Power & Energy Soc. IEEJ., No.115.

[4] Yoitsu Sekiguchi, Hitoshi Nojo, Noriyuki Ohkawa, Satoru Hashimoto, 2007, "*A Study on Recycling Technology of Cross-Linked Poly-Ethylene Part 2*", The 2007 Annual Meeting Report IEEJ., No.7-173.