

Development of a XLPE insulating with low peroxide by-products

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ABSTRACT

The chemically crosslinked polyethylene (XLPE) is widely used in MV/HV insulating due to its good electrical properties and good thermomechanical behavior. However as a result of the chemical crosslinking, the gas and polar by-products from the peroxide are generated. The presence of such gas modifies the interface pressure between cable and pre-molded accessories which could lead to partial discharge generation allowing to the dielectric breakdown. The degassing of insulating is a key parameter for the reliability of the cable system. Furthermore, the polar by-products influence electrical properties under DC stresses. The purpose of this paper is to present a new XLPE with very low content of by-products fulfilling the standard requirement regarding crosslinking density.

Keywords

Crosslinking, Hot Set Test, Co-agent, By-product

INTRODUCTION

Although Low Density Polyethylene (LDPE) has very good electrical properties, it is not suitable for high power cables due to its temperature of operation which is limited to 70°C. This problem can be solved by crosslinking. Radical reaction with organic peroxides is one of the most widely used crosslinking methods to enhance the insulation ability to withstand high temperature.

However, crosslinking generates volatiles and no volatiles by-products. The gas released need to be removed from the cables for safety reasons, mechanical considerations (high pressure on the interface to the accessories) and electrical reasons (risk of partial discharges). Degassing or thermal treatment is an important step for cable manufacturing process. This step needs several days of heating depending on the insulating thickness and the length of the insulated cable core.

As example, the effect of degassing is illustrated in Fig. 1 in case of crosslinked polyethylene. FTIR analysis shows that an important proportion of acetophenone and cumyl alcohol can be removed by degassing the sample for 2 days at 50°C.

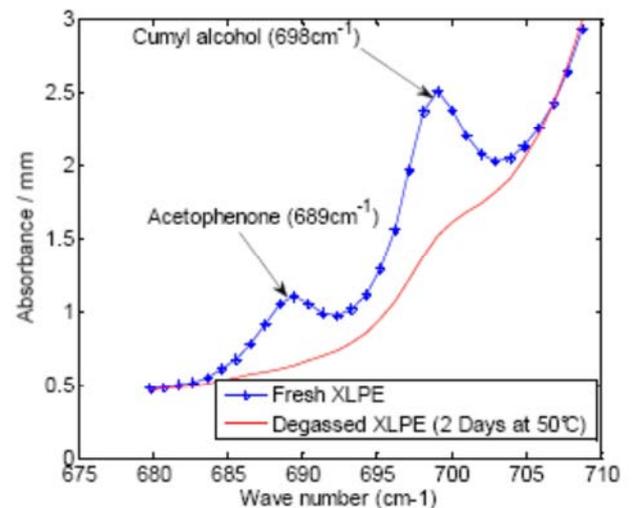


Fig. 1: FTIR spectrum of degassed and non-degassed XLPE samples crosslinked .

In case of dicumyl peroxide, high boiling point substances such as acetophenone, cumyl alcohol and alpha-methyl styrene remain in the insulation for a long time and are thought to assist the transport of charges by introducing a certain level and number of traps in the insulation bulk.

To minimise the impact of by-products, additives are often used. The performances of XLPE can also be improved through the reduction of the concentration of high boiling point by-products residues. This can be achieved by using a suitable crosslinking agent.

This paper reports a new crosslinking network where the overall by-products content before degassing step has been dramatically reduced compared to standard crosslinked polyethylene.

EXPERIMENTAL INVESTIGATIONS

Organic additives-polyethylene mixtures are prepared by absorption process. A rheometer is used to monitor the cure characteristics of the compounds through the value of the torque (Mh = lb.inch). The crosslinking density is measured thanks to the hot set test value at 200°C under 0,2 MPa. The crosslinking assessment has been explored on sample crosslinked at 200°C for 10 minutes. The gas content was measured by gas chromatography from crosslinked pellets under nitrogen atmosphere for 10 minutes at 190°C. The content of polar by-products is measured by chemical extraction with a solvent followed by gas chromatography.

RESULTS AND DISCUSSIONS

Many studies [1-4] have demonstrated the interest of using crosslinking co-agents to improve the mechanical properties of elastomers. The co-agents are polyfunctional molecules which are highly reactive in the presence of free radicals and are grafted on the elastomeric chains to form a very dense crosslinking network.

The restriction of the amount of by-products released during the crosslinking passes through the decreasing the peroxide amount. However, such approach cannot give any guaranty to ensure a satisfactory level of crosslinking while added co-agents to a mixture of peroxide and PE (LDPE) allow reaching the appropriate crosslinking level.

a) Nature of the co-agent exploration

The co-agents studied are classified into two types. Type I co-agents contain acrylates functions and type II co-agents are characterized by allylic functions.

The below table shows the crosslinking density values (Mh) according to the nature of the co-agent. The values are compared with a standard blend which contains no co-agent but only peroxide.

co-agent	type Co-agent	reactive functions	Mh (lb.in)
-	-	-	2,8
A	I	2	0,9
B	I	2	1,1
C	I	3	1,7
D	II	3	2,3
E	II	3	2,7

The crosslinking density increases with the number of reactive function of co-agent. Additionally it is noted that the tri-functional type II co-agents are more efficient than type I.

The combination of a reduced concentration of peroxide with an appropriate added type II co-agent can be considered as an innovative way to reduce significantly the by-products content and maintaining a satisfactory crosslinking level.

b) Nature of the peroxide exploration

To investigate the influence of the chemical structure of the peroxide with the addition of a crosslinking type II co-agent, several families of peroxides have been tested.

The various mixtures explored contain peroxide with same content, the co-agent E and a polyethylene (LDPE).

peroxide	molar content peroxide (mmol)	Mh (lb.in)
P1	3	1,9
P2	3,8	2,5
P3	2,7	2,8

Although the molar concentration was the lowest, the peroxide P3 provides the highest crosslink density.

From the above table, we determined the optimum content peroxide P3 in order to have a Mh≈2,5 (it's the usual value for PE to have good crosslinking density). We compared the value to the standard compound with optimized Mh (≈2,5 lb.in).

We determined the concentrations of gas (methane, ethane) and polar by-products (ketone and alcohol).

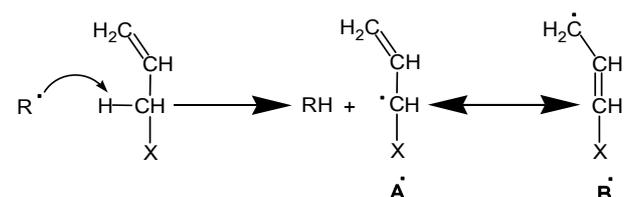
Peroxide	Co-agent E	Hot set Test (%)	gas	Polar by-product
P2	no	55	<800	<12000
P3	yes	65	<500	<6000

We note even with less peroxide content than standard compound, we got a satisfying value of Hot Set Test. In addition, the gas content and Mh polar by-products decreased significantly.

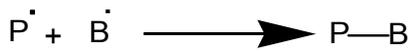
Type II co-agents being less polar than type I co-agents their chemical compatibility with the polyethylene are improved [5-8].

Type I co-agents contains unsaturations which will react by addition reactions with the corresponding peroxide radicals (RO[•]) and the macro radical polymer (P[•]) to form either grafting reactions of 1, 2 or 3 vinyl functions of the co-agent on the polymer (crosslinking reaction) either homopolymerization reactions of co-agent [9-11]. This latter reaction limits the effectiveness of the polyethylene crosslinking reaction in the presence of co-agent.

Type II co-agents are characterized by allylic function and thus the presence of very labile hydrogen [5]. This will generate abstraction reactions of extractable allylic hydrogen (scheme 1) and additions reactions [12]. The allylic radical formed is stabilized by resonance.



(R[•] = radical peroxide and/or other radicals)

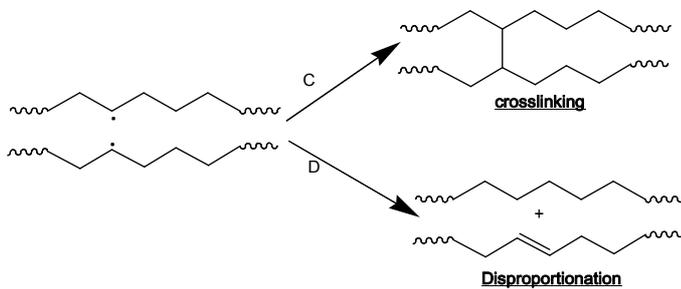


(P = macro radical polymer)

Scheme 1

So the allylic radical is less reactive next to addition reactions and thus the homopolymerization reaction of type II co-agents is less compared to the type I co-agents. The grafting reactions are improved.

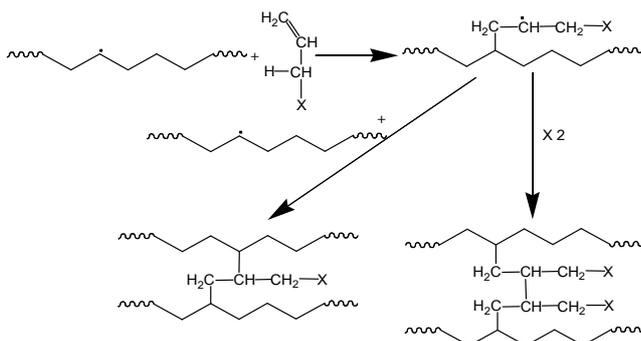
During the crosslinking reaction of the PE, the macroradical P° may react according to 2 antagonistic reactions. The first is the combination 2 macroradicals (way C) and 2nd the disproportionation reaction (way D) (scheme 2) [11].



Scheme 2

The reaction way C enables to crosslink the polymer while that of the way D regenerates two polymers units whose one contain an ethylenic link.

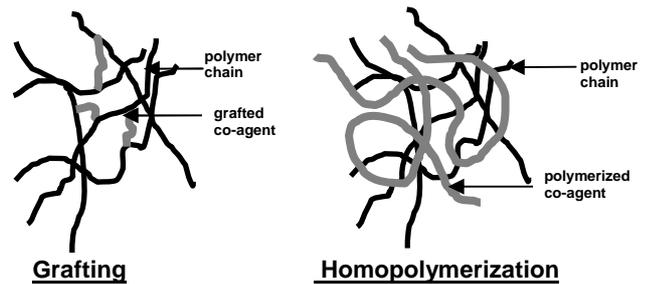
The introduction of allylic co-agent in the reaction mixture generates radical adducts that are able to react only by combination reactions (scheme 3) [13].



Scheme 3

Co-agent will therefore stabilize the macroradical polymer and cancel the disproportionation reaction.

So, the crosslinking mechanism of the PE in the presence of co-agents may be described as the result of the grafting reactions of the polymer and by reactions of homopolymerization of the co-agents molecules which will penetrate in the three dimensional network and strengthen the material (scheme 4) [14-17].



Scheme 4

c) Study of the nature of polyethylene

Previous results are obtained from a LDPE. It is known that linear low density polyethylenes (LLDPE) are more reactive with the crosslinking. We compared the reactivity of a LLDPE in the presence of co-agents.

With this family of polyethylene, it is usually considered that the torque (Mh) to be of the order of 3,5 lb.inch for a hot set test <100%. All studied mixtures contain the same molar amount of co-agent, an antioxidant and the polymer.

PE Structure	peroxide P3 content (%)	co-agent	Mh (lb.In)	Hot Set Test (%)
LDPE	C	E	2,5	67
LLDPE	C/2	E	3,9	40
LLDPE	C/2	C	2,6	195

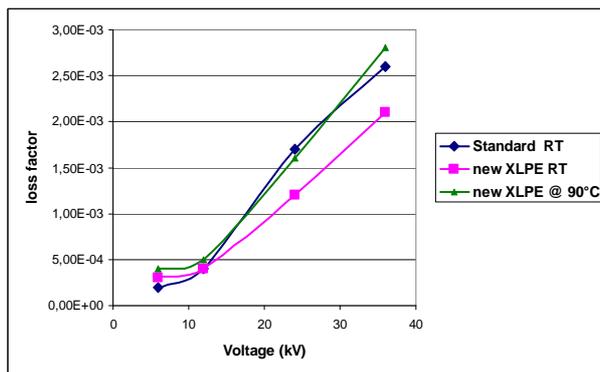
We note that with LLDPE and co-agent E we can further decrease the content of peroxide with a good crosslinking density. In addition, we observe, as in the case of LDPE, the acrylate co-agent type I are not sufficiently effective.

For the compound LLDPE+ co-agent E, we measured a scorch time at 140°C of 53 minutes which is a satisfactory value. This mixture does not present a risk of scorch during extrusion. So we made a medium voltage insulating NF C 33-226 12/20 (kV).

From the extruded insulating, we measured different physico-chemical properties.

Mh (lb.in)	3,5
Hot Set Test (%)	58
Initials mechanicals properties	
Tensile strength (MPa)	29
Elongation at break (%)	660
Ageing 7 days 135°C	
ΔTS (%)	1,3
ΔEB (%)	15
Ageing 20 days 150°C	
Tensile strength (MPa)	27
Elongation at break (%)	638

We have also measured on the same material the electrical properties such as dielectric loss (graph 1), the relative permittivity and the breakdown voltage. The values obtained are compared to the standard insulating. Both insulatings were degassed in the same conditions.



Graph 1

	standard RT	new XLPE RT	New XLPE @ 90°C
Relative permittivity ϵ_r	2,4	2,3	2,1
Breakdown voltage	>15 U ₀	>15 U ₀	-

We observe that the new material has at room temperature lower dielectric loss values than the standard material.

At the service conditions (90°C), the dielectric losses for the new material are equivalent to those of the standard material at room temperature.

The values of relative permittivity and breakdown voltage are satisfying.

CONCLUSION

We found that the type II co-agents are more efficient next to the crosslinking of polyethylene than the type I co-agents. The combination of a peroxide and type II co-agent allowed to reduce significantly peroxide content with a good crosslinking density (Hot Set Test <175%).

The contents of polar by-products and gas are decreased significantly.

This new material had good physico-chemical and electrical properties.

This new material opens interesting prospects in particular to reduce the degassing time of medium voltage insulating for submarine cable and for high voltage cable for DC application.

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