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TITLE : **MINERAL FILLER AND POLYMER MATRIX COMPATIBILISATION
FOR PERFECTING MATERIALS USED AS INSULATION AND
SHEATH OF ELECTRICAL CABLES**

PROJECT
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MINERAL FILLER AND POLYMER MATRIX COMPATIBILISATION FOR PERFECTING MATERIALS USED AS INSULATION AND SHEATH OF ELECTRICAL CABLES

1. ABSTRACT

Due to strong environmental concerns, substitution of polyvinylchloride (PVC) by an halogen-free thermoplastic is a major target in the wire industry. In addition to an halogen-free composition, the new material must exhibit a high elongation at break together with a sufficiently high ultimate tensile strength, a low production cost of production and an high enough fire resistance, so to compete advantageously with PVC wires. In order to impart fire resistance to the polymer matrix, we have to add a fire retardant filler, such as magnesium hydroxide produced at a low cost by a european producer. The envisioned mechanical properties for the final composites are an ultimate tensile strength of 12.5 MPa and an elongation at break of 125 %.

Although fine solid particles (fillers, pigments,...) can be mechanically dispersed within a previously melted polymer, performances of the final dispersions strongly depend on the interactions between the solid particles and the polymer matrix. Chemistry of the interface is thus of a crucial importance for the production of high quality products.

The main problem is the compatibilisation between polymer matrix and filler in order to get an homogeneous compound ; commercial compatibilizers and polymeric compatibilizers synthesized at UNIVERSITY OF LIEGE are studied for this aim.

This research leads us to select Ethylene Vinyl Acetate (EVA), Linear Low and Very Low Linear Density Polyethylene (LLDPE and VLDPE) as polymer matrix ; Hydrofy N 2,5 µm and Hydrofy 1 P/N 1,5 µm are choosen as filler.

A commercial compatibilizer gives us the required compound ; compatibilizers synthesized at UNIVERSITY OF LIEGE with high Tg (so easy to handle) and a not to high molecular weight give us promizing results but their synthesis need to be optimize.

2. INTRODUCTION

The electric cable industry has to manage the evolution of its cables for different reasons :

- For ecological reasons, the choice is now to underground cables instead of overhead cables in order to respect environmental ; so, we can think that future cable will be produced in bigger quantities, and will use cheaper materials.

- The necessity is now to avoid any kind of pollution of environment due to cable during its life service or after its use ; so cable makers will have to decrease their PVC consumption and will have to know how to eliminate cables after use.

- The severity of the new reglementations concerning security of people induces to avoid cable which propagate flame and give toxic and corrosive smokes.

So the aim is to have materials used in cable industry and other industries with the following characteristics :

- No pollution, no toxicity, no corrosivity
- . Low cost, less than the actual products
- Capacity of production quickly available in Europe.

In the future, the results should be applied to the sheath of the european industrial cable 1000 V, which is one of the most important market in the cable field, about 300 MECU of cable and 10 % for the sheath.

3. TECHNICAL DESCRIPTION

The objective of this study is to elaborate an halogen free material for cable sheathing exhibiting good mechanical properties, flame resistance, and a low cost ; the filler used to fireproof the base polymer is a magnesium hydroxide supplied by our partner SIMA : this european sea water precipitated grade is less expensive than the $Mg(OH)_2$ grade based on a mineral raw material : 0,45 ECU/kg compared to about 2,5 ECU/Kg.

The required specifications are :

- Good processability
- Tensile strength: $T_s \geq 10$ Mpa
- Elongation at break: $E_b \geq 125$ %
- The cable must hold the vertical flame test (generally a wire holds this test when the oxygen index of the material is about 27- 28).
- Evolution after thermal ageing (7 days 100°C) $\Delta T_s \leq 25$ %
 $\Delta E_b \leq 25$ %
- Evolution after oil immersion test (4 h 70°C) $\Delta T_s \leq 40$ %
 $\Delta E_b \leq 40$ %
- The material must be recyclable
- Price : about 1 ECU/l.

To reach this aim, several types of polymer matrix are tested such as EPR or EPDM, EBA or EMA, LLDPE or VLDPE, and EVA ; several fillers from NUOVA SIMA have to be evaluated. In order to well mixed the polymer matrix and the filler to get an homogeneous compound, we test in a first part different commercial compatibilizers.

In the second step of this study, several polymeric compatibilizers synthesized at UNIVERSITY OF LIEGE are tested. The general basic assumption is that a properly tailored block or graft copolymer is able to strongly anchor a filler ($Mg(OH)_2$) to polyethylene (PE) and, accordingly, to provide the final composite with sufficiently high elongation at break (125†%) and ultimate tensile strength (12.5MPa). A priori, the block or graft copolymer should combine a constitutive component selectively interacting with the filler surface (the anchoring block) with a second component identical to or miscible with the polyethylene matrix (the stabilizing block). The best LIEGE compatibilizers are selected to produced an industrial compound.

4. RESULTS

4-1. Polymer selection

Regarding the required specifications - flexibility, mechanical properties, raw material cost - the polyethylene and its copolymers are the most suitable materials for this application. Different preliminary tests have been performed to select the polymers :

- ***EPR OF EPDM***

These polymers do not hold the oil immersion test

Almost EPR or EPDM polymers are packed in balls so they are difficult to introduce in a continuous mixer.

- ***EBA or EMA***

They do not hold the oil immersion test and they cannot accept large amount of filler.

These two base polymers have been forsaken for the following tests

- ***LLDPE***

The less expensive one but it does not accept large filler amount ; moreover it can be used in association with different polymers to decrease the material cost.

- ***VLDPE***

The VLDPE are in fact heterogeneous ethylene-alkene copolymers with very low density and wide melting range temperatures : these copolymers are more expensive than LLDPE but they accept larger filler content ; the VLDPE used in all the first experiments is the Norsoflex 2230 from ENICHEM ; in a second stage and in order to increase the tensile strength different VLDPE will be tested.

- **EVA**

The EVA are ethylene vinyl acetate copolymers ; there are a large range of materials and many suppliers in Europe ; the price of the EVA depends on the V.A. amount: a copolymer with 26°/0 VA represents a good compromise between price and filler acceptance ; these polymers give materials with higher Oxygen Index than PE base formulation.

- **Maleic anhydride grafted polymers**

These polymers contain a carboxylic acid group capable of reacting with the filler ; these polymers more expensive than the non-grafted ones can be used as formulation base polymers or as compatibilizing agents.

Preliminary tests have been carried out with maleic anhydride grafted EVA as base polymers : the obtained materials have good tensile strength but a very low elongation at break ; the strong interaction between the polymer and the filler would be responsible of this low elongation (analysis by infrared spectroscopy).

These grafted polymers will not be used as base polymers in the following experiments.

4-2. Filler selection

We have to choose a filler with a high flame retardancy, a low cost, while allowing good mechanical properties and a high extrusion speed ; the fire behaviour depends on the filler characteristics, the finer filler producing the highest effect.

Three different particle size magnesium hydroxides have been supplied by SIMA and tested : **hydrofy 0,7-1,5 and 2,5 µm.**

The Mg(OH)₂ 0,7 µm is the most efficient but also the most expensive Mg(OH)₂ and it reduces the mechanical properties of the blend, so the major experiments have been carried out with Mg(OH)₂ 1,5 µm and Mg(OH)₂ 2,5 µm.

4-3. Industrial results

The industrial trials are processed from the optimised formulations obtained in laboratory.

The two selected fillers are :

- HYDROFY 1P/N 1,5 µm.

- HYDROFY N 2,5 µm.

which are the two magnesium hydroxyde fillers which give the best results.

The selected polymers are :

- EVA copolymers (Ethylene Vinyl Acetate) such as
ELVAX 260 and ELVAX 265 from DUPONT

- LLDPE or VLDPE (Linear Low or Very Low Density Polyethylene) such as
LL1 001 from EXXON and LL1004 from EXXON
FW 1600 from ENICHEM
ENGAGE 8003 from DOW

The compounds are produced in an internal mixer, The polymer is introduced at first, compatibilizer and magnesium hydroxyde are introduced after ; the extrusion is made on 1.5 mm² copper wire.

4-3-1 **Additives commercially available**

4-3-1-1 **Silane coupling agents**

The industrial results obtained on wire are compared to the laboratory results.

We can notice a decreasing of the elongation at break after ageing ; because of the high price of this kind of compatibiliser, this way is forsaken.

4-3-1-2 **Maleic Anhydride Polymers**

As compatibilizer, we select the EPR grafted maleic anhydride VA 1801 from EXXON, which gives the best results in laboratory.

Two first compounds are produced with HYDROFY 1P/N 1.5 µm.

The first one is made with NORSOFLEX FW 1600 (MFI = 0,9- d = 0,910) from ENICHEM, which is cheaper than NORSOFLEX 2230, and ELVAX 265 from DUPONT as basic polymers.

The second one is made only with NORSOFLEX FW 1600 in order to decrease the price of the compound.

The extrusions, made on 1.5 mm² copper wire, gave a very smooth surface.

The results are presented on table 1 ; these two compounds fullfill all the requirements with a price of about 1.1 ECU/1.

A third compound is produced with HYDROFY N 2,5 µm ; the produced compound also fullfills all the requirements.

4-3-2 LIEGE **compatibilizing** agents

It would be much too longer to present all the results obtained at UNIVERSITY OF LIEGE ; among the so many compatibilizers synthesized at LIEGE, we present here after the most interesting results.

Industrial trials are produced with the compatibilizers from UNIVERSITY OF LIEGE,

Two first compounds are made with two optimised compatibilizers synthetised by LIEGE.

Two other compounds are produced with the same compatibilizers synthetised by an industrial producer IVEA EMAILLAGE ; this society placed in MEZIEU, near LYON, is a subsidiary of ALCATEL CUIVRE ; it is specialised in the production of insulating polymers deposited in very thin thickness on copper wire used for electric motors.

The results obtained, with the first two compounds made with the compatibilizers from LIEGE are presented table 2. The compatibilizer is a poly-N-butylacrylate MCGU-C-35 from LIEGE.

We can see that the initial and after ageing mechanical characteristics on moulded plates are very closed to the laboratory results ; however we can notice a very strong decrease of the tensile strength when measured on cable compared to the measurement on plate. We can observe small porosities on the extruded compounds ; this porosity appears during the extrusion and it is due to the evaporation of the remaining solvent (dioxane) used for the synthesis of the compatibilizer. This porosity is the explanation of this difference of tensile strength at break between moulded plates and cable. Except the tensile strength at break the other requirements are fulfilled.

A second compound is made with an other compatibilizer from LIEGE MCGU-D 26, which is a Poly Methacrylate of N Butyl. This compatibiliser is solid at ambient temperature and its use is easier.

We can notice that the results are very close to the first one, and the same decreasing of the tensile strength on wire is observed, All the other requirements are fulfilled.

Two other compounds are produced with the compatibilizers from the society IVEA EMAILAGE, the results are presented on table 3. The results are very close to the laboratory results ; except the low tensile strength measured on wire, all the other characteristics full-fill the requirements.

The price of the raw material (acrylate of N butyl) is about 2,3 ECU/1 and so the price of the compatibilizer should give us a price in the objective of 1 ECU/l for the final compound (for comparison, the price of the compatibiliser VA 1801 is about 3,8 ECU/kg and ist rate in the formulation is double -15 phr for VA 1801 compared to 7 phr for LIEGE compatibiliser).

5. CONCLUSION

It is shown that low cost halogen free materials for wires and cables applications can be developed.

Two fillers are selected HYDROFY N 2,5 μm and HYDROFY 1P/N 1,5 μm .

Several types of polymers are tested such as EPR or EPDM, EBA or EMA, LLDPE or VLDPE, and EVA ; Ethylene Vinyl Acetate (EVA), Linear Low and Very Low Density Polyethylene (LLDPE, VLDPE) are selected for industrial trials.

Several kinds of commercial compatibilizers are tested in laboratory, the best ones being choosen for industrial productions.

First industrial trials are produced with silane coupling agents ; despite of a good surface aspect and good initial mechanical characteristics, these compatibilizers are forsaken because of a decreasing of the elongation at break after ageing, and because of the price compared to the objective.

Other industrial trials are produced with a commercial maleic anhydride grafted polymer as compatibiliser, VA 1801 from EXXON. Two compounds are produced with HYDROFY 1P/N 1,5 μm and a third one with HYDROFY N 2,5 μm , and all together fullfill the requirements with a price of 1,1 ECU/1.

Compatibilisers from LIEGE are produced by a industrial partner, IVEA EMMAILLAGE, and are tested in compounds. The extrusions give a very good aspect surface. We can notice the very high elongation at break, between 400 and .500 % on cable. All the other characteristics are fulfilled except the tensile strength at break which is low on cable compared to the measurements on moulded plates.

This lower tensile strength at break measured on cable is due to the evaporation during the extrusion of the remaining solvent contained in the compatibilizer. This evaporation induces porosity in the cable and decreases the mechanical characteristics, specially the tensile strength at break. A better drying of the compatibilizer with stronger evaporation of the solvent during the synthesis should increase the tensile strength at break.

These new compatibilizing agents synthesised by the University of Liege are very promising but their development and the elaboration would require more time in order to improve the conditions of synthesis for a better drying to evacuate all the solvent ; this should increase the tensile strength at breakup to the required compound.

6. ACKNOWLEDGMENTS

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TABLE 1

INDUSTRIAL TESTS

	Laboratory Results	Industrial Results	Industrial Results	Requirements
NORSOFLEX FW 1600 EVA 265 VA 1801 HYDROFY 1 P/N 1,5µ IRGANOX 1010	70 20 10 140 0,5	70 15 15 160 1	85 15 160 1	
MOONEY VISCOSITY(1+4)-150°C		91	78	
OXYGEN INDEX % FLAME TEST-CE1332-PartI	29,5	29 Pass	27 Pass	28 Pass
MECHANICAL CHARACTERISTICS TENSILE STRENGTH MPa ELONGATION AT BREAK %	16,1 148	14,8 134	12,6 141	≥12,5 ≥125 %
THERMAL AGEING 7D 100°C TENSILE STRENGTH MPa ATS ELONGATION AT BREAK % AEB	18,6 16% 145 -2%	18,2 23% 125 -7%	14,2 13?io 139 -1?40	≤±25% ≤±25%
OIL IMMERSION 4H 70°C TENSILE STRENGTH MPa ATS ELONGATION AT BREAK % AEB	14,6 -10% 140!0 -5%	12 -19% 1231% -8%	12,3 -2% 154% 9%	≤40% ≤±40%
ANGULAR TEAR STRENGTH N/mm	63	53	54	≥30

TABLE 2

	Laboratory Results	Industrial Results	Industrial Results	Requirements
LL 1001 ENGAGE 8003 MCGU - C 35 * MCGU - D 26 ** HYDROFY N 2,5pm IRGANOX 1010	70 30 7 160 0,5	70 30 7 170 0,5	70 30 7 170 0,5	
MOONEY VISCOSITY(1+4)-150°C		21	22	No requirements
OXYGEN INDEX % FLAME TEST-CEI 332-Part 1	25	24 Pass	26 Pass	Pass
MECHANICAL CHARACTERISTICS <u>On moulded plates</u> TENSILE STRENGTH MPa ELONGATION AT BREAK % <u>On wire</u> TENSILE STRENGTH MPa ELONGATION AT BREAK%	10,1 680% +/-20	9,5 591% 5,1 426%	8,1 568% 5,1 330%	≥ 12,5 ≥ 125% ≥ 12,5 ≥ 125%
THERMAL AGEING 7D 100°C <u>On moulded plates</u> TENSILE STRENGTH MPa ATS ELONGATION AT BREAK % AEB <u>On wire</u> TENSILE STRENGTH MPa ATS ELONGATION AT BREAK % AEB	9,3 -8% 640% +/-40 -6%	8,1 -15% 623% -5%	6,7 -17% 448?40 -21% 5,2 1% 263% -20%	≤ ±25% ≤ ±25% ≤ ±25% ≤ ±25%
OIL IMMERSION 4H 70°C <u>On moulded plates</u> TENSILE STRENGTH MPa ATS ELONGATION AT BREAK% AEB		6 -37% 671 % 14%	5,5 -32% 640% 13%	≤ 40% ≤ 40%
ANGULAR TEAR STRENGTH N/mm	24,3	47	45	≥ 30

* MCGU - C 35 = Polyacrylate of N Butyl - Mn = 10000- Mw / Mn = 12,3

** MCGU - D 26 = PolyMethacrylate of N Butyl - Mn = 21000- Mw / Mn = 2,7

TABLE 3

	Laboratory Results	Industrial Results	Industrial Results	Requirements
LL 1001 ENGAGE 8003 * MCGU - C 35 **Compatibilizer IVEA EMAILLAGE HYDROFY N 2,5pm IRGANOX 1010	70 30 7 160 0,5	70 30 7 170 0,5	100 7 170 0,5	
MOONEY VISCOSITY(1+4)-150°C		19	19	No requirements
OXYGEN INDEX % FLAME TEST-CE1332-PartI	25	25 Pass	25 Pass	No requirements Pass
MECHANICAL CHARACTERISTICS <u>On moulded plates</u> TENSILE STRENGTH MPa ELONGATION AT BREAK % <u>On wire</u> TENSILE STRENGTH MPa ELONGATION AT BREAK%	10,1 680% +/-20	7,7 549% 5,2 493%	9,6 615?4. 5 552%	≥ 12,5 ≥ 125% ≥ 12,5 ≥ 125%
THERMAL AGEING 7D 100°C <u>On moulded plates</u> TENSILE STRENGTH MPa ΔTS ELONGATION AT BREAK % AEB <u>On wire</u> TENSILE STRENGTH MPa ATS ELONGATION AT BREAK% AEB	9,3 -8% 640% +/-40 -6%	7,5 -3% 598% 10%	7,9 -18% 498% -1 9%	≤ ±25% ≤ ±25%
OIL IMMERSION 4H 70°C <u>On moulded plates</u> TENSILE STRENGTH MPa ATS ELONGATION AT BREAK % AEB		4,8 -38% 554?40 1%	6,3 -34% 736% 20%	≤ 40% ≤ 40%
ANGULAR TEAR STRENGTH N/mm	24,3	40	31	≥ 30

* MCGU - C 35 = Polyacrylate of N Butyl - Mn = 10000- Mw / Mn = 12,3

**Compatibilizer IVEA EMAILLAGE = Polyacrylate of N Butyl - Mn = 8000- Mw I Mn = 6,7