

Reuse of XLPE on a LLDPE Matrix: Assessment of the Mechanical Properties Comparing with Predication Models

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Abstract

ALCOBRE is a big copper wire manufacture. On is manufacture process, to obtain the electrical insulation, a XLPE (cross-linked linear polyethylene) thermoset polymer is used as coating external layer. The wastes of this polymer can't be discarded with regular industrial waste, and the costs of disposing of them in landfills are significant. The XLPE needs to be segregated and then a certified waste company transports this waste to identified dumping areas.

In this work we try to reuse some of this XLPE waste by the incorporation on a LLDPE (linear low-density polyethylene) matrix. The LLDPE/XLPE blend can be used on the insulation of some copper wires and in this case is possible to reduce the waste level and decreases the waste costs.

To assess the compatibility of these two polymers several LLDPE/XLPE blends were made and mechanically tested. After, the analysis of the experimental data, was made recurring to different predication models of blended polymers such us: the rule of mixtures, Kerner-Uemura-Takayanagi model, and Nicolai-Narkis model.

The comparison will allow to assess the adhesion between the two material phases.

The results anticipate a good adhesion between both phases. For the tensile modulus, a linear relationship is found, which indicates a good adhesion between the phases along the composition range. The increase of XLPE in the mixture decreases the bending and tensile stress. For tensile stress, the Nicolai-Narkis model is suitable for modelling behaviour by inducing good adhesion between phases.

In relation to the modulus, it is possible to verify that in relation to the bending modulus the incorporation of XLPE does not affect the module. However, the tensile modulus will be affected with the XLPE quantity in the mixture.

Keywords: Mechanical Characterization, Polymer Blend, Thermoset Resin, Waste Add-value, Industrial Wastes.

Introduction

Thermoset resins are cross-linked and cannot be remoulded, in contrast to thermoplastic which can easily be remelted. Some of the thermoset resins can be converted relatively easily to new reactive intermediates, such as polyurethane [1]. However, the more common thermosetting resins are not practical to depolymerize to their original constituents.

The reuse and the recycling of thermoset resins are one problem that a lot of industries are dealing with. The thermoset resin wastes generated in the production lines drive to a financial cost of disposal these kinds of wastes on landfills.

Recycling of thermoset resin materials will contribute to the sustainability of industrial processes. Nowadays a wide type of engineering materials is recycled to a great extent. However, thermoset materials, as a special category of engineering materials have not yet been properly recycled. Recycling will eventually lead to resource and energy savings for production [2].

At present, there are very limited commercial recycling operations for mainstream thermoset resin products, due to technological and economic constraints [2].

Recently, several techniques have been developed to induce the depolymerization of thermosetting resins contained in composite materials to make them recyclable [3].

Instead of recycling the thermosets using a heavy chemical process, the industry is trying to reuse the thermosets into new applications. Several studies are being made to characterize and optimize this reuse. [3, 4].

Low-density polyethylene (LDPE) is used for more than 60 years for several applications. Nowadays, however, for some special applications, LDPE has been replaced by crosslinked polyethylene (XLPE) [5, 6]. XLPE is common to use to coat electrical cables due to the insulation properties. Nevertheless, this material suffers from its environmental impact because there is a high level of greenhouse gas emission during its manufacture and a low level of recyclability at the end of its lifetime due to chemical crosslinking.

Therefore, developing new recyclable polyethylene insulating materials substituting the conventional XLPE has been becoming a long-standing topic [7]. Polymer blending has been proved to be an effective and noteworthy approach for material modification for a variety of properties [7].

Thermoplastic polymer blends are considered as a new type of environmental-friendly cable insulation material substituting XLPE, which exhibits lower energy consumption in the production process and better recyclability at the end of service life. This has triggered increasing research interests in the past two decades [7].

Polyethylene (PE) is one of the highly utilized polymers in daily life. The application of PE ranges from food packaging containers to parts of aircraft. For packaging applications, Low-density polyethylene (LDPE) and Linear low-density polyethylene (LLDPE) are most commonly used [8-11].

Due to the chemical compatibility, in this work, XLPE will be reused as a filler on an LLDPE matrix, to assess the correlation between the XLPE incorporation and the final mechanical properties

Methods

The LLDPE used is commercialized under the trade name HF2007.

The LLDPE is after, transformed into XLPE using a reagent commercialized under the trade name LE 4423.

In this work, it was used the XLPE resultant of the waste of an insulation cooper wire production line crushed into a Moretto plastic shredder due to the hardness of the plastic. After that, the XLPE was ground in a Piovon RSPB 20 mill.

The samples were obtained by extrusion. The blend ratio has been achieved recurring to a Moretto gravimetric doser that feeds a Maillefer MXC80-30D extruder. The extrusion temperature profile was established by combining the melting temperature of the polymers, the degradation temperature, and the extrusion conditions suggested by the supplier's datasheet. The extrusion temperature profile is presented in figure 1.

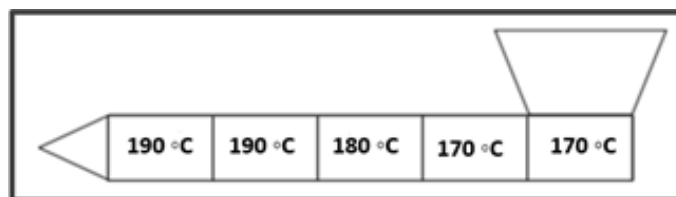


Figure 1: Extrusion temperature profile

Four different samples were prepared based on mass fraction: LLDPE/XLPE [70:30], [50:50], [10:90] and neat XLPE [0:100].

The extruded blend has been cut in the form of specimens with the following dimensions (according to the respective standard):

Flexural specimens: 20 x 100 x 2 mm³ prismatic bars;

Tensile specimens: dog-bone-shaped specimen with a reference cross-section of 4 x 2 mm² and 25 mm length; and a grip cross-section of 12,5 x 2 mm² and an overall length of 75 mm.

The assessment of the mechanical properties was made recurring to tensile and flexural tests.

To measure the tensile properties according to ISO 527 standard a universal mechanical testing machine Shimadzu AG-X (Shimadzu Corporation – Scientific Instruments, Japan) 100 kN was used. A crosshead velocity of 2 mm/min was used, and the tests were performed in a standard laboratory atmosphere of 23 ± 2 °C and 50 ± 5% relative humidity. A grip distance of 50 mm was used. The envisaged tensile properties assessed were the Modulus, Maximum stress, and the strain at break. At least 9 specimens were tested for each blend composition.

To measure the flexural properties according to ISO 14125 standard a universal mechanical testing machine Shimadzu AG-X (Shimadzu Corporation – Scientific Instruments, Japan) 100 kN was used. A 3-point flexural test has been used with a crosshead velocity of 3,5 mm/min and span of 60 mm. The tests were performed in a standard laboratory atmosphere of 23 ± 2 °C and 50 ± 5% relative humidity. The envisaged flexural properties assessed were the Modulus, Maximum stress, and the strain at break. At least 9 specimens were tested for each blend composition.

The obtain data was analysed using predication models for polymer blends.

The mechanical properties of the blends (indicated by the subscript b) can be predicted by models assuming different interfacial behaviours between phases:

Well-disperse phases with perfect adhesion (ROM) spherical inclusions of one polymer in a continuous polymer matrix with perfect adhesion or no adhesion (KUT) spherical inclusions with variable interphase interactions, ranging from poor to good adhesion (NN).

These models will be described in the following once they will be used to interpret the adhesion between the polymer phases within the XLPE/LLDPE blend.

ROM Model

The rule of mixtures considers a perfect adhesion between the matrix (subscript m) and the dispersed phase (subscript d) and a perfect dispersion of the spherical inclusions in the matrix. This model can be used to predict the modulus (eq.1) and the tensile stress (eq.2) of the blend, as described:

$$E_b = \left(\left[\frac{E_d}{E_m} - 1 \right] \times \phi_d + 1 \right) \times E_m \quad (\text{eq.1})$$

$$\sigma_b = \left(\left[\frac{\sigma_d}{\sigma_m} - 1 \right] \times \phi_d + 1 \right) \times \sigma_m \quad (\text{eq.2})$$

Where E_b is the modulus of the blend, E_d is the initial modulus of the disperse phase, E_m is the modulus of the matrix, ϕ_d is the weight fraction of the disperse phase, σ_b is the maximum stress of the blend, σ_d is the maximum stress of the disperse phase and σ_m is the maximum stress of the matrix.

KUT Model

The KUT Model treats the blends as spherical inclusions of one polymer, having a modulus of E_d , in a continuous matrix another polymer having a modulus E_m . The Poisson's ratio of the matrix (ν_m) is taken to be 0.5 [12]. This model has two variations. One assumes perfect adhesion (eq.3) at the blend interface and the other assumes no adhesion at all. (eq.4)

$$E_b = E_m \left(\frac{(7 - 5\nu_m)E_m + (8 - 10\nu_m)E_d - (7 - 5\nu_m)(E_m - E_d)\phi_d}{(7 - 5\nu_m)E_m + (8 - 10\nu_m)E_d - (8 - 10\nu_m)(E_m - E_d)\phi_d} \right) \quad (\text{eq.3})$$

$$E_b = E_m \left(\frac{(7 - 5\nu_m)E_m - (7 - 5\nu_m)E_m\phi_d}{(7 - 5\nu_m)E_m - (8 - 10\nu_m)E_m\phi_d} \right) \quad (\text{eq.4})$$

NN Model

In the NN Model, the interphase interaction constant, K , is a function of the blend structure. For spherical inclusions, $K = 1.21$ stands for the extreme case of poor adhesion. The inter-phase adhesion takes place for values of $K < 1.21$. When $K = 0$, the adhesion is sufficient so that the polymer matrix strength will not decrease due to blending, meaning that $\sigma_b = \sigma_m$. Is possible to achieve that better adhesion occurs when K is low [12].

The NN model assumes that both phases are of a no adherent type and the maximum stress is a function of either the area fraction or the volume fraction of the dispersed phase. The NN model is given by:

$$\sigma_b = (1 - K\phi^{2/3}) \quad (\text{eq.5})$$

In this work, the calculation of K values by adjusting equation 5 to the experimental data gives a measure of the adhesion between both phases.

In table 1, the various models used, the conditioning of each, and what analysis can be carried out through the results obtained are presented.

Table 1: Models used in this work to interpret blend structure

| Model | Equation | Blend Structure | Interpretation | Use |
|-------|-------------|--|---|--|
| ROM | (1) and (2) | Spherical polymer inclusions in a continuous polymer matrix with perfect adhesion | perfect adhesion and dispersion | Fit to the model for E and σ |
| KUT | (3) and (4) | Spherical polymer inclusions in a continuous polymer matrix with perfect adhesion or no adhesion | (a) perfect adhesion (b) no adhesion | Fit to the model for E |
| NN | (5) | Spherical inclusions with variable inter-phase interactions, ranging from poor to good adhesion | K —interphase interaction constant, function of the blend structure | K adjustment for σ values: $K=1.21$ —no adhesion $K<1.21$ —phase's adhesion $K=0$ —no property decrement |

Results

The main properties of the used two polymers are presented in Table 2 and were obtained by the technical datasheet provided by the raw-material supplier.

Table 2: Raw material main properties values.

| | LLDPE | XLPE |
|----------------------------------|------------|----------|
| Melt temperature (°C) | 180-210 | 150-170 |
| Degradation temperature (°C) | 230 | 200 |
| Tensile elongation at break (%) | 1260-1530 | 300 |
| Tensile strength at break (MPa) | 40-45 | 15 |
| Tensile Modulus (MPa) | 190-210 | 190-210 |
| Density (g/cm ³) | 0.920 | 0.923 |
| Flexural Modulus (MPa) | 1100 | 171 ± 45 |
| Flexural elongation at break (%) | 1950 ± 100 | 439 ± 30 |
| Flexural strength at break (MPa) | 56 ± 3 | 21 ± 1 |

The results of the tensile tests of LLDPE/XLPE blends are given in Table 3.

Table 3: Tensile properties of LLDPE/XPLE blends.

| LLDPE/XLPE Blend (mass fraction) | Maximum Stress [MPa] | Tensile Modulus [MPa] | Strain at maximum stress [%] |
|----------------------------------|----------------------|-----------------------|------------------------------|
| 70:30 | 28.96 ± 1.5 | 142.4 ± 14 | 3.39 ± 0.3 |
| 50:50 | 24.46 ± 2.2 | 117.4 ± 16 | 1.72 ± 1.2 |
| 10:90 | 16.38 ± 1.2 | 156.0 ± 31 | 0.21 ± 0.1 |
| 0:100 | 15.50 ± 0.4 | 162.0 ± 28 | 2.14 ± 0.1 |

Based on the predictive models, the estimated Tensile modulus is presented in table 4.

Table 4: Predicted Tensile Modulus.

| LLDPE/XLPE Blend (mass fraction) | ROM [MPa] | KUTPerfect adhesion [MPa] | KUTno adhesion [MPa] |
|----------------------------------|-----------|---------------------------|----------------------|
| 70:30 | 195.6 | 194.6 | 122.1 |
| 50:50 | 186 | 184.8 | 60.4 |
| 10:90 | 166.8 | 166.3 | 136.5 |
| 0:100 | 162 | 162 | 162 |

Figure 2 shows the evolution of the modulus with the XLPE mass fraction, based on the data from tables 3 and 4.

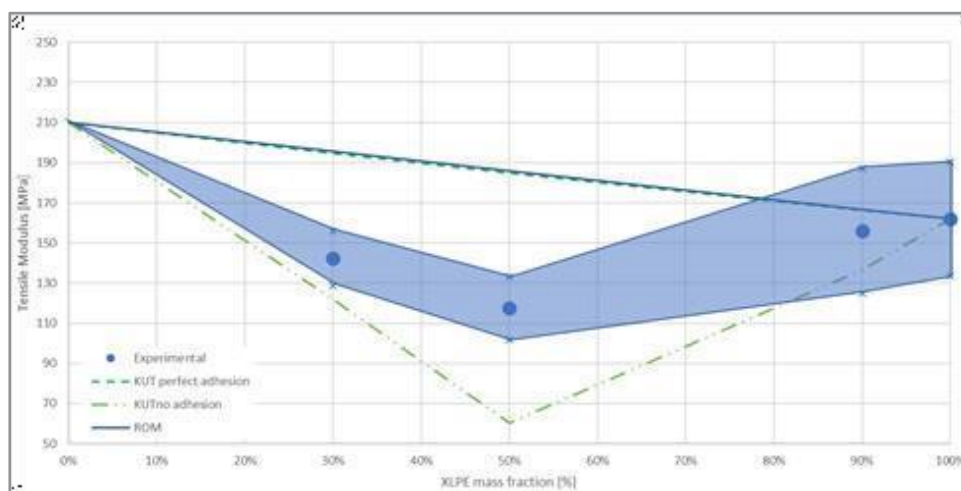


Figure 2: Tensile modulus, E, results and predicted values from models

Is possible to verify that the incorporation of XLPE on an LLDPE matrix will affect the tensile modulus. Analysing the data two main issues can be observed: (i) the KUT with perfect adhesion and the ROM models do not give a good prediction of E; (ii) the KUT with no adhesion model doesn't give a good prediction but presents the same evolution for E (decreasing until 50% of XLPE incorporation, and then increasing until 100% of XLPE).

This analysis suggests that the adhesion of the two phases increases for higher incorporation of XLPE. The maximum stress of the blends can also be estimated from the above-presented prediction models. From the NN model, the parameter K can be calculated, giving estimations of the interphase interaction. The calculated values are expressed in table 5 and result from the matching of the experimental data to the model results.

Table 5: Adjusted values for K for LLDPE/XLPE Blends

| LLDPE/XLPE Blend (mass fraction) | K (NN model) |
|----------------------------------|--------------|
| 70:30 | 0.795 |
| 50:50 | 0.725 |
| 10:90 | 0.682 |
| 0:100 | 0.656 |

As shown in table 5, K values are always lower than 1,21, meaning that good adhesion between phases is achieved. The decreasing of K value with the incorporation of XLPE suggests that the adhesion between the two phases increases with the incorporation of XLPE.

Table 6 presents the predictions of the tensile stress for ROM and NN (with different K) models for the considered LLDPE/XLPE blends.

Table 6: Models predictions of maximum stress

| LLDPE/XLPE Blend (mass fraction) | ROM | NN | | |
|----------------------------------|-----|-----|--------|--------|
| | | K=0 | K=0.71 | K=1.21 |
| 70:30 | 36 | 45 | 30.7 | 20.6 |
| 50:50 | 30 | 45 | 24.9 | 10.7 |
| 10:90 | 18 | 45 | 15.2 | |
| 0:100 | 15 | 45 | 13.1 | |

Figure 3 shows the variations in the tensile maximum stress with the mass fraction of XLPE and respective model predictions.

The increase of XLPE on the blends results in a general decrease in the maximum stress of the blends. The NN model, with the adjusted K, fits well with the experimental data.

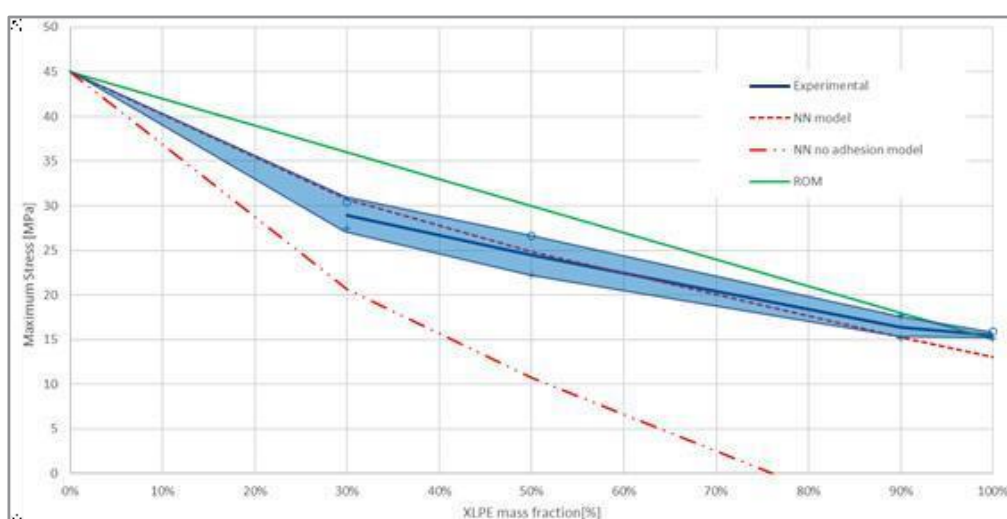


Figure 3: Maximum Stress results and predicted values from models.

The results of the flexural tests of the blends are given in table 7.

Table 7: Flexural properties of LLDPE/XLPE Blends

| LLDPE/XLPE Blend (mass fraction) | Maximum Stress [MPa] | Flexural Modulus [MPa] | Strain at maximum stress [%] |
|----------------------------------|----------------------|------------------------|------------------------------|
| 70:30 | 10.84 ± 0.76 | 305.1 ± 20.8 | 4.91 ± 1.1 |
| 50:50 | 11.52 ± 1.89 | 204.5 ± 11.2 | 6.60 ± 0.7 |
| 10:90 | 8.46 ± 1.42 | 208.9 ± 23.3 | 6.32 ± 2.1 |

Figure 4 shows the variations in Eb with the incorporation of XLPE and respective model predictions.

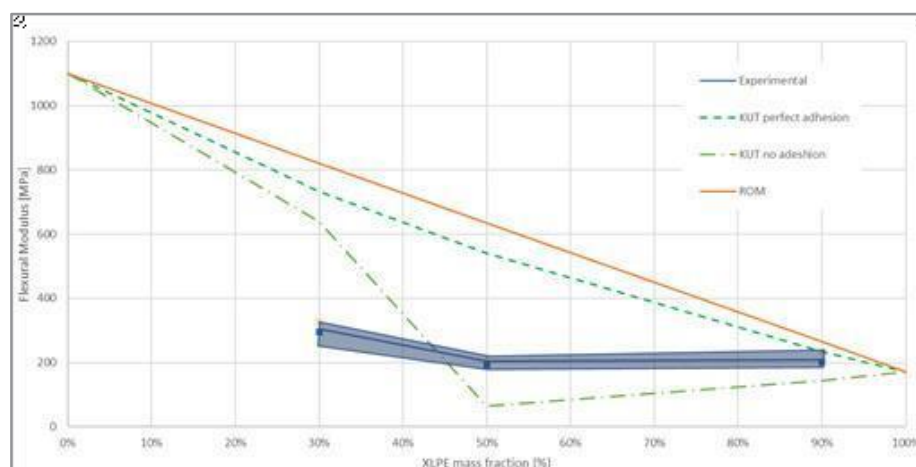


Figure 4: Flexural Modulus results and predicted values.

Conversely to the tensile modulus, the variation of the modulus with the XLPE mass fraction is almost irrelevant. It is also possible to verify that the models cannot adjust the value of the Modulus.

Conclusions

The properties of blended polymers can be tailored to achieve a given performance. LLDPE/XLPE blends over a large set of compositions were investigated in this work. The blends were extruded, and their mechanical (tensile and flexural) behaviours were assessed. The increment of XLPE on the blend decreases the flexural and tensile stress. For the tensile stress, the Nicolai-Narkis model is suitable to model the behaviour denoting a good adhesion between phases.

Regarding the modulus, it is possible to verify that the flexural modulus presents a small variation related to the incorporation of XLPE. However, the tensile modulus will be affected with the amount of XLPE presented in the blend.

Analysing the preliminary results, it is possible to state that, probably, in specific applications, the use of thermoset XLPE in a blend with LLDPE and therefore reduce the waste of XLPE.

Next studies will focus on the influence of XLPE on the impact and thermal behaviour of the blend.

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