# Polyamide 12 Filled with Cross-Linked Polyethylene Waste: Processing, Compatibilization, and Properties

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Cross-linked polyethylene (XLPE) is primarily used as a coating and insulator for electrical wires and cables. The cross-links render recycling through remelting unfeasible, and XLPE waste is usually incinerated or sent to landfills. Previous investigations showed that XLPE increased the impact strength of commodity thermoplastics. Hence, incorporating XLPE in polyamide 12, an engineering thermoplastic, was studied using maleic anhydride grafted polyethylene (PE-g-MA). Formulations were prepared using a co-rotating twin-screw extruder containing 20 wt% XLPE with 0, 2, 4, and 8 wt% compatibilizer. Test specimens were injection-molded. DSC results showed that adding XLPE and compatibilizer reduced PA12 crystallinity but affected little melt and crystallization temperatures. Morphological analyses revealed poor adhesion between polyamide 12 and XLPE, which improved when adding PE-g-MA. The lack of adhesion when XLPE is added strongly reduces the mechanical properties, except for impact strength, which increased by ca.120% compared to the formulation without XLPE; while using 4 wt% compatibilizer this increase was ca. 140%. When adding PE-g-MA as a compatibilizer, some recovery was achieved in tensile strength and strain at break, and impact strength increased furthermore. Flexure and HDT tests showed a decrease in stiffness after adding XLPE. Stiffness was further reduced in compositions containing compatibilizer.

Keywords: Polyamide 12, XLPE, Reuse, Waste, Compatibilization.

## 1. Introduction

Topics related to polymer recycling have been increasingly studied, not only for environmental reasons but also to reduce the cost of the final product and modify properties, among others. Recycling thermosets encounters a much greater technical challenge and less commercial success compared to recycling thermoplastics<sup>1</sup>. One such thermoset is cross-linked polyethylene (XLPE), widely used as an insulator and coating in medium and high-voltage wires and cables. The cross-links change polyethylene's behavior from thermoplastic to thermoset, thus making recycling difficult<sup>2,3</sup>, and XLPE waste is normally sent to landfills or incinerated<sup>4</sup>.

One of the ways to reuse plastic waste is to incorporate them into thermoplastic matrices, thus forming blends or composites with these materials<sup>5</sup>. In recent years, many investigations have been carried out seeking the incorporation of XLPE in thermoplastic matrices, which are chemically similar to XLPE<sup>4,6-9</sup>. For example, Freitas and Bonse<sup>10</sup> assessed, in 2017, the effect of XLPE waste particle content and size on the engineering properties of HDPE. The influence of each parameter was assessed using a 2<sup>2</sup> factorial design with a central point for contents of 1 wt% and 9 wt% XLPE and an average particle size of 74 and 842 µm. The XLPE content had the strongest influence on the investigated properties, and a higher content resulted in a significant increase in impact strength and a decrease in flexural strength, tensile strength, flexural modulus, and heat deflection temperature (HDT). The increase in particle size increased impact resistance, with a reduction in the strain at break and in the flexural modulus. It was also shown that the interaction between particle size and content reduces impact strength and tensile modulus. As expected, due to the chemical similarity between the polymer matrix and the dispersed phase, SEM analysis indicated strong adhesion between XLPE and HDPE.

Some works were also developed focusing on incorporating XLPE waste in chemically different polymer matrices, not only in polyethylene matrices. Moraes and Bonse<sup>11</sup>, in 2017, added XLPE waste in a PP/EPDM/talc matrix at 10, 20, and 30 wt%. Mechanical tests showed a decrease of approximately 25% in tensile strength, about 90% for elongation, and 60% for elastic modulus. The impact strength was also reduced by about 60% compared to the formulation without XLPE. Flexural strength and modulus were reduced by around 24 and 34%, respectively. SEM analyses indicated weak adhesion between the matrix and XLPE, with several gaps at the interface between the matrix and the dispersed phase.

In 2018, Lindqvist et al.<sup>12</sup> incorporated XLPE waste in PP homopolymer at 25 and 50 wt%. Waste from the electrical cable manufacturing process (A) was mixed with post-consumer electrical cable waste (B). The average cross-link densities were, respectively, 75 and 52%. As the XLPE content increased, stiffness and tensile strength decreased. Strain at break decreased by 65% and 48% with the addition of 25 wt% and 50 wt% XLPE, respectively. The impact strength increased by 85% with the addition of

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50 wt% XLPE. The source of the XLPE waste did not result in significant variations in the mechanical properties of the specimens obtained. Also, in this study, an aging test carried out at 105 °C showed materials maintain their properties for at least 2880 hours. Based on the tests, the author estimated a useful life of these compounds of at least 50 years at 25 °C.

Silva<sup>13</sup> also analyzed, in 2018, the use of XLPE waste as an impact modifier in polypropylene using an ethylenepropylene copolymer (EPM) as a compatibilizer. Formulations containing 5, 15, and 25 wt% XLPE and 4, 6, and 8 wt% EPM were obtained by two different types of processing: direct extrusion of all components and premixing of XLPE and EPM in a mixing chamber followed by extrusion with the PP. Processing with the premix proved to be more effective in dispersion and homogeneity, promoting the coating of the XLPE particles by the EPM. Such dispersion and homogeneity were proven in the strain at break and SEM analysis. The obtained micrographs showed weak adhesion between the matrix and dispersed phase and the presence of fibrils. Impact strength had a maximum increase of 50%, but all other properties decreased with the incorporation of XLPE, with or without the compatibilizer. EPM acted more strongly as an impact modifier than as a compatibilizer.

A thermoplastic that might benefit from XLPE waste incorporation is polyamide 12 (PA12). PA12 is an engineering thermoplastic belonging to the polyamide family<sup>14-18</sup>. Due to its structure, it has a lower concentration of amide groups in its macromolecule than typical polyamides<sup>14,17</sup>, the result of which is that its properties represent a valuable combination between the properties of typical polyamides and polyolefins, such as low water absorption, causing its physical properties to change little in applications where humidity varies; good chemical resistance; excellent resistance to impact and high modulus of elasticity<sup>19</sup>.

Typically, PA12 compounds are more expensive than other polyamides. Thus, its use is restricted to specific applications, such as fuel pipes and other fluids for the automotive and aerospace industries or applications that require dimensional accuracy in water distribution systems<sup>20-22</sup>. In addition, recently, PA12 has become the most used polymer material in the manufacture of prototypes for industries in different segments using multi-jet fusion technology<sup>23</sup>.

The present work analyzes the technical feasibility of incorporating 20 wt% of XLPE waste in a PA12 matrix. As there is little chemical similarity between the matrix and the dispersed phase, a compatibilizer is required<sup>5</sup>. To compatibilize the resulting compound, maleic anhydride grafted polyethylene (PE-g-MA) at three different concentrations (2, 4, and 8 wt%) were assessed.

PE-g-MA was chosen as a compatibilizer because the maleic anhydride (the polar fraction of PE-g-MA) can react with the amino group present in the polyamide. At the same time, the nonpolar moiety of PE-g-MA has a chemical affinity with the polyethylene, thus forming an interface with improved adhesion between the polyamide and polyethylene phases<sup>24-26</sup>.

The novelty of this investigation resides in the fact that the polymer system we investigated has yet to be dealt with in the literature. As mentioned, most studies reusing crosslinked polyethylene waste as a filler have used commodity plastics as matrices. Our research has already used polyamide 6, an engineering thermoplastic, as a matrix. However, this is the first time PA12 has been used. It should be mentioned that PA12 has a lower concentration of amide groups in its macromolecule than typical polyamides, such as PA6. Hence its properties represent a valuable combination of the properties of typical polyamides and polyolefins. Reducing the cost of PA12 compounds by using XLPE residues may greatly expand applications of this engineering thermoplastic.

## 2. Experimental

### 2.1. Materials

The PA12 used as a matrix under the trade name Vestamid® L2140, was supplied in pellets by Evonik Industries AG, with a density of 1010 kg/m<sup>3</sup>, melt volume-flow rate (275°C/5.0kg) of 36 cm<sup>3</sup>/10 min, and melting point 178 °C (DSC).

The XLPE waste came from an electrical wire and cable coating industry and was donated by FAEX Soluções Ambientais. In a previous study, this waste was micronized to an average particle size of  $500\mu$ m. The FTIR analysis performed by Silva<sup>13</sup> on this material shows that this polyethylene probably underwent crosslinking via silane.

The PE-g-MA used in preparing the formulations was supplied by the Dow Chemical Company under the tradename Fusabond® M603, with a density of 940 kg/m<sup>3</sup> and melt mass-flow rate (190°C/2.16kg) of 25 g/10 min.

## 2.2. Methods

#### 2.2.1. Incorporation of XLPE into PA12

PA12 was dried in a Vacucell VUS-B2V-M vacuum oven at 80 °C for 10 hours. After drying, PA12, XLPE, and compatibilizer were tumble mixed prior to extrusion. The mixtures were fed to a HAAKE extruder, model Polylab Rheomex OS PTW6, with a co-rotating twin-screw (L/D = 25, D = 16 mm). The rotation speed used was 400 rpm and the temperatures in the barrel were gradually increased from 220 °C in the feed zone to 240 °C in the dosing zone.

After extrusion and pelletizing, the pellets were again dried in a vacuum oven at 80 °C for approximately 10 hours before injection molding to manufacture test specimens. The injection-molding machine used was an HM 60/350 Battenfeld. The barrel temperature was maintained between 250 and 275 °C, and the mold temperature was 70 °C. The injection and holding pressure were maintained at 1000 and 800 bar, respectively. The parameters used were the same for all formulations, both for neat PA12 and the remaining compounds. Seven formulations were prepared, as shown in Table 1. Formulation PA12 refers to P12 pellets not subjected to extrusion, only injection-molded, whereas PA12-EXT refers to PA12 pellets extruded and injection-molded. To verify the effect of PE-g-MA alone on the PA12 matrix, a formulation containing an intermediate content to those used to compatibilize XLPE with PA12 was prepared, i.e., PA12/PE-g-MA5.

## 2.2.2. Characterization

To assess the effect of XLPE addition to PA12 and its compatibilization the following tests were carried out: XLPE

Formulation		PA12 (%)	XLPE (%)	PE-g-MA (%)
1	PA12	100	-	-
2	PA12-EXT	100	-	-
3	PA12/PE-g-MA5	95	-	5
4	PA12/XLPE20	80	20	-
5	PE-g-MA2	78	20	2
6	PE-g-MA4	76	20	4
7	PE-g-MA8	72	20	8

Table 1. Formulations investigated in the current study.

particle size analysis; scanning electron microscopy (SEM) analysis; heat deflection temperature (HDT); differential scanning calorimetry (DSC); thermogravimetric analysis (TGA); and mechanical testing (tensile, flexural and impact). Test specimens were conditioned in an environment with a controlled temperature of 21 °C and relative humidity of approximately 50% for at least 48 hours prior to testing, which was performed under the same conditions.

### 2.2.2.1. Particle size analysis of XLPE

The particle size of micronized cross-linked polyethylene was measured using a Microtrac Bluewave laser particle analyzer in dry mode. An airflow is generated that drags the particles from the sample holder to the detector, after which an XLPE particle size distribution curve is generated.

#### 2.2.2.2. Scanning electronic microscopy (SEM) analysis

The morphologies of fractured surfaces of the test specimens ruptured at room temperature in the impact test were analyzed by scanning electron microscopy (SEM) in a Zeiss Auriga field emission gun scanning electron microscope. The fractured surfaces were gold-coated and images were obtained at 5.0 kV using secondary electrons. PA12, PA12-EXT, and PE-g-MA8 formulations were analyzed.

## 2.2.2.3. Heat deflection temperature measurements (HDT)

In accordance with ASTM D648-18 standard<sup>27</sup>, three specimens of each formulation were tested in the edgewise position until a deflection of 0.25 mm in a silicon oil bath. The applied stress at the center of the specimens was constant and equal to 1.82 MPa, the distance between supports was equal to 100 mm, and the heating rate was 2 °C/min. The tests were carried out using an Instron Ceast 6-Station HDT & Vicat Tester.

### 2.2.2.4. Differential Scanning Calorimetry (DSC)

DSC analyses were performed according to ASTM D3418-15<sup>28</sup> to identify variations in the transition temperatures and degree of crystallinity of the compatibilized and noncompatibilized PA12/XLPE compounds compared to neat PA12. The degree of crystallinity of PA12 was determined according to Equation 1, in which *w* is the mass fraction of PA12 in the sample,  $\Delta$ Hf is the melting enthalpy of PA12 in the sample and  $\Delta$ Hf° is the melting enthalpy of the 100% crystalline polymer<sup>14</sup>. In the case of PA12, the value used for  $\Delta$ Hf° was 209.3 J/g<sup>29</sup>.

$$\%_C = \frac{\Delta H f}{w \times \Delta H f^{\circ}} \times 100 \tag{1}$$

The test was carried out in a model Q100 TA Instruments equipment under the following conditions: Initial equilibrium at 0 °C, a heating rate of 10 °C/min up to 220 °C under nitrogen gas flow of 50 mL/min. 1-minute isotherm. Cooling from 220 °C to 0 °C at a heating rate of 10 °C/min. Second heating ramp at the same conditions as the first one. The sample mass was between 5 and 10 mg.

### 2.2.2.5. Thermogravimetric Analysis (TGA)

TGA analysis was performed according to ASTM E1131-08 to identify variations in the decomposition temperature of the different compounds.

The test was carried out in an SDT Q600 TA instruments equipment. The heating rate was 20 °C/min, with a temperature range from 25 to 600 °C under a constant nitrogen flow rate of 100 mL/min, with a sample mass between 10 and 20 mg.

### 2.2.2.6. Tensile testing

The tensile tests were performed using a 5567 Instron Universal Testing Machine, following the criteria specified in the ASTM D638-14<sup>30</sup>. To determine yield strength, tensile strength, toughness, and strain at break tests were carried out on five specimens of each formulation, stretched to rupture at a speed of 50 mm/min, using a distance between grips of 50 mm and an extensometer with a 500% maximum strain.

To determine Young's Modulus, five other specimens of each formulation were tested at a crosshead speed of 5 mm/ min up to 2% strain. A 50 mm extensometer with a 10% strain capacity was used, allowing one to collect more points at the elastic region of the stress-strain curve. The modulus was then obtained from the slope of the straight line formed between 0 and 0.3% strain.

### 2.2.2.7. Impact testing

First, seven specimens of each formulation were notched with a V-notch, at an angle of 45° from the center of the notch and 2 mm deep. The equipment used for this step was a C-6898-000 Instron CEAST motorized notching machine.

The Charpy impact test was carried out following the criteria established by ASTM D6110-18<sup>31</sup> at room temperature (23 °C) and with a 5.4 J pendulum using an Instron CEAST 9050 pendulum impact testing machine.

#### 2.2.2.8. Flexural testing

Three-point bending tests were performed in an Instron 5567 Test Machine, in accordance with ASTM D790-17<sup>32</sup>. The test speed was 1.3 mm/min and the span between supports was 50 mm. Flexural modulus at 0.3% strain and flexural strength at 5% strain were collected.

## 3. Results and Discussion

## 3.1. Particle size distribution analysis

As mentioned in the materials section, XLPE has been used in other research and was previously micronized to an average size of 500  $\mu$ m. Analysis was performed to confirm the average particle size to be incorporated into PA12. The particle size distribution curve (Figure 1) shows particles ranging from 26 to 2000  $\mu$ m. Particles smaller than 200  $\mu$ m and larger than 1000  $\mu$ m represent 17% of the sample. The three highest incidence points are 418, 497, and 591  $\mu$ m, totaling about 40% of the particles.

The importance of particle size was shown in previous studies by Freitas and Bonse10, who found that at low XLPE waste content (1 wt% - 9 wt%) when the average particle size of XLPE increased from 74 to 842 µm in an HDPE matrix, impact strength increased. In contrast, the tensile strain at break and flexural modulus decreased. However, in another study on the effect of XLPE particle size by Leite<sup>33</sup>, who incorporated XLPE waste in an HDPE matrix at higher contents, i.e., 15 wt%, with average particle sizes of  $400 \,\mu\text{m}$ ,  $1300 \,\mu\text{m}$  and a  $50/50 \,\text{mixture of these two (bimodal}$ distribution), the formulation containing 1300 µm particle size XLPE showed higher flexural strength and elastic modulus, however a slightly lower impact strength, and a strain at break around 25% lower; possibly, due to the larger particles having a reduced surface area, and consequently less interaction between the dispersed phase and the matrix, resulting in more stress concentrators, i.e., the larger particles caused a more premature rupture. Hence in the current study an average particle size closer to 400 µm was selected.

## 3.2. Scanning Electron Microscopy (SEM)

Fractured surfaces of the test specimens ruptured at room temperature in the impact test were analyzed by SEM. Figure 2 shows a comparison between the fracture surfaces of the specimens. Even at low magnification, it is clear that the addition of XLPE to the PA12 matrix caused a fracture with greater surface irregularity. This effect seems to be less pronounced for formulations containing XLPE into which the compatibilizer was added.

Figure 3 shows micrographs of the fractured surfaces at higher magnification. The micrograph of the PA12 formulation, as expected, shows a very homogeneous surface. The micrograph of the PA12/XLPE20 formulation shows a heterogeneous surface with high deformations. It is also possible to notice the presence of voids, which before the impact were occupied by XLPE particles that were pulled out, indicating poor adhesion between the matrix and the dispersed phase. This poor adhesion was expected, as PA12 and XLPE are not chemically similar. Soares<sup>34</sup> also identified a lack of adhesion between polyamide 6 and XLPE, characterized by the presence of gaps between the matrix and the dispersed phase and voids in the matrix.

When 8 wt% PE-g-MA is added, the morphology of the PE-g-MA8 formulation became more uniform. The deformations appear smaller and the number of voids present on the surface also decreased, suggesting a better bonding of the dispersed phase with the matrix.



Figure 1. Particle size distribution curve of the micronized XLPE waste.



**Figure 2.** Micrographs of impact test fractured specimens of PA12: neat; with 5 wt% PE-g-MA; with 20 wt% XLPE; with 20 wt% XLPE + 8 wt% PE-g-MA (magn:16x).

## *3.3. Heat Deflection Temperature (HDT)*

Figure 4 shows the heat deflection temperatures of PA12 and the different PA12 compounds. Since PA12 is stiffer than XLPE, it needs a higher temperature to undergo thermal deflection. The tensile modulus of XLPE, about 200 MPa<sup>35</sup>, and of PA12, about 1800 MPa (obtained in the current study) are clear evidence that PA12 is many times stiffer than XLPE. The presence of XLPE in PA12 should then result in a less rigid compound, which requires a lower temperature to undergo deflection, as observed in the studies of Freitas and Bonse<sup>10</sup> and Soares<sup>34</sup>. When XLPE was added to the PA12 matrix, there was actually a reduction of approximately 7% compared to the neat polyamide.

The addition of 2 wt% PE-g-MA maintained the heat deflection temperature without significant variations. With the increase in PE-g-MA content, the temperature progressively decreases until a reduction of 19% compared with the value of the non-compatibilized compound. This result suggests that the addition of PE-g-MA in the PA12 matrix reduces the stiffness of the compound, consequently reducing the thermal deflection temperature. The reduction in PA12 stiffness with the addition of PE-g-MA is corroborated by the tensile modulus





Figure 3. SEM micrographs (magn:100x) of: a) neat PA12; b) PA12 containing 20 wt% XLPE without compatibilizer; c) PA12 containing 20 wt% XLPE with 8 wt% compatibilizer. Different size particles are circled for better visualization.

results presented later in section 3.6.1, which show that a 5 wt% addition of PE-g-MA reduces PA12 tensile modulus from 1.84 GPa to 1.34 GPa. This effect can be attributed to the flexible PE backbone of PE-g-MA, as it consists of only simple carbon-carbon bonds in the main chain.

### 3.4. Differential Scanning Calorimetry (DSC)

The DSC technique allowed obtaining the values of the degree of crystallinity, melting temperature  $(T_m)$ , and crystallization temperature  $(T_c)$  of each of the formulations. The results of the degree of crystallinity of PA12 are shown in Figure 5, whereas  $T_m$  and  $T_c$  are listed in Table 2.

The solid and striped bars shown for each formulation in Figure 5 refer to the first and second heating run results, respectively. For all compositions, the degree of crystallinity for polyamide 12 in the second run was slightly higher than in the first run. The degree of crystallinity in the first run refers to the crystallinity of the injection-molded specimens. In contrast, the second run refers to the crystallinity obtained after constant rate cooling of the sample melted in the first run. The constant cooling rates in the DSC tests are lower than those in the injection-molding process. As Brydson<sup>15</sup> described, lower cooling rates facilitate the movement of polymer chains to form larger crystallinity in PA6 injection-molded specimens when the mold temperature increased, i.e., when the cooling rate was lower.

Figure 5 also reveals an increase of approximately 10% in the degree of crystallinity of the extruded PA12 (PA12-EXT) compared to the non-extruded polyamide (PA12). The extrusion process has probably caused chain scission in PA12, decreasing



**Figure 4.** Heat deflection temperatures for the different PA12 formulations.



Figure 5. DSC PA12 degree of crystallinity of the investigated PA12 compounds (solid bars:1<sup>st</sup> heating; striped bars: 2<sup>nd</sup> heating).

the average chain size and facilitating the formation of polymer crystals. This phenomenon, described by Gilbert<sup>35</sup>, was also observed by Teotonio<sup>37</sup> in her study on the incorporation of nano calcium carbonate in PA12.

Formerulation	T <sub>m</sub> (°C)		T (%C)
Formulation –	1 <sup>st</sup> heating	2 <sup>nd</sup> heating	$I_{c}(C)$
PA12	175.7	177.6	153.2
PA12-EXT	175.7	176.0	150.2
PA12/PEgMA5	176.3	175.2	152.7
PA12/XLPE20	176.4	175.3	151.1
PEgMA2	177.0	177.2	150.2
PEgMA4	175.6	175.1	152.7
PEgMA8	175.8	175.3	151.2

Table 2. DSC melt (T<sub>m</sub>) and crystallization (T<sub>c</sub>) temperatures of PA12 in each formulation.

Comparing PA12-EXT with PA12/PEgMA5 and PA12/ XLPE, all of which underwent the same extrusion and injection processes, reveals that adding 5 wt% compatibilizer and 20 wt% XLPE to PA12 reduced the degree of crystallinity by approximately 26% and 15%, respectively. These reductions can be explained by the fact that specific impurities and additives, except for nucleating agents, tend to reduce the degree of crystallinity because they hinder regular packing and hence interfere with the crystallization ability of the polymer<sup>14</sup>. The degree of crystallinity of the PA12/XLPE compounds compatibilized with 2, 4, and 8 wt% (PEgMA2, PEgMA4, PEgMA8) was also lower than that of the extruded PA12.

As shown in Table 2, the crystalline melting temperatures for PA12 are in the range of 175 °C to 177 °C, very close to that found in the literature for PA12, for example, by Canevarolo<sup>14</sup>, and within the range specified by the supplier, i.e., 175 °C to 181 °C. The T<sub>c</sub> results for the different formulations show that the crystallization temperatures of the polymer matrix are between 149 °C and 153 °C. Both T<sub>m</sub> and T<sub>c</sub> results are very close to the results found by Teotonio<sup>37</sup> for PA12, i.e., 178 °C and 152 °C, respectively.

The addition of XLPE and compatibilizer did not significantly affect either the melting temperature or the crystallization temperature of PA12. As reported by Soares<sup>34</sup>, the addition of XLPE and PE-g-MA also did not cause significant changes in the melting temperature of another polyamide, PA6.

### 3.5. Thermogravimetric Analysis (TGA)

TGA enabled assessing weight loss as a function of temperature for the different PA12 formulations. The TGA thermograms reveal two main events. The first one, a slight weight loss at approximately 180 °C, is attributed to the release of volatiles, including moisture. The second one, above 400 °C with weight losses of up to almost 100%, is attributed to the decomposition of the polymers. As the TGA curves of the formulations are very similar, an amplified region is presented in Figure 6 to distinguish the curves more clearly. The far-right curve corresponds to the PA12 formulation, and the far-left one to the PA12 formulation containing 20 wt% XLPE compatibilized with 8 wt% PE-g-MA. TGA curves are typically shifted to the right when thermal stability increases. Hence, adding XLPE to PA12 reduces PA12's thermal stability slightly, which is aggravated by adding PE-g-MA.



Figure 6. Amplified region of TGA weight loss curves for the different PA12 formulations.



Figure 7. Bar graph of TGA  $T_{onset}$  and  $T_{max}$  for the different PA12 formulations

TGA also enabled assessing the temperature at which, for each compound, the decomposition begins  $(T_{onset})$  and the temperature at which the decomposition rate is maximum  $(T_{max})$ . The temperatures  $T_{onset}$  and  $T_{max}$  are shown in Figure 7. The solid bars refer to  $T_{onset}$ , while the striped bars refer to  $T_{max}$ .

The results of  $T_{onset}$  for the various formulations vary between 438 °C and 458 °C. Comparing the values of the compositions PA12-EXT and PA12/XLPE20, adding 20 wt% XLPE waste does not promote a significant difference in the temperature at which the decomposition event begins. A slight variation in  $T_{onset}$  can be seen when the compatibilizer is added. However, the temperatures differ by a maximum of 6 °C in comparison with the PA12/XLPE20 formulation, suggesting that adding the compatibilizer impacts only slightly the thermal stability of the compound.

The results also show that the  $T_{max}$  did not change significantly with the addition of XLPE and compatibilizer.

The PA12 formulation, which was not processed by extrusion, had a slightly higher  $T_{max}$  than the other formulations. According to Gilbert<sup>35</sup>, some polymer degradation mechanism is more likely in the extrusion process (high temperatures and shear rates). This slightly higher  $T_{max}$  for this formulation may be related to the absence of the extrusion step.

## 3.6. Mechanical properties

## 3.6.1. Tensile testing

Figure 8 shows the stress-strain curves representing the formulations: extruded PA12; PA12 with 5 wt% PE-g-MA; PA12 with 20 wt% XLPE; PA12 with 20 wt% XLPE containing 2 wt%, 4 wt%, and 8 wt% PE-g-MA. Apparently, the addition of XLPE to PA12 caused a great reduction in the mechanical properties and the use of the compatibilizer promoted a partial recovery of these properties.

The mean values and the respective standard deviations of the tensile strength results are shown in Figure 9. For the compositions without XLPE, the tensile strength was considered the maximum stress in the yield region, which occurs around 10% of strain, and not the maximum stress on the curve just before failure. This stress peak occurs due to the occurrence of the high orientation of the polymer chains at high strains, thus increasing the tensile strength (strain hardening) just before break.



Figure 8. Representative stress-strain curves of PA12 and PA12 compounds.



Figure 9. Bar graph of tensile strength results for PA12 and its different compounds.

Based on the results obtained, a slight increase is noted in the tensile strength of the extruded PA12 compared to the PA12 that did not undergo extrusion. The increase in this property is probably related to the increase in the degree of crystallinity after the extrusion process, as evidenced by the DSC results. It is known that with an increase in the degree of crystallinity, there is an increase in yield strength and elastic modulus<sup>34</sup>.

It can also be seen that adding 20 wt% XLPE waste in the PA12 matrix resulted in a drop of approximately 36% in tensile strength compared to the result obtained for PA12 extruded without filler. The studies by Silva<sup>13</sup>, Lindqvist et al.<sup>12</sup>, and Soares<sup>34</sup>, who dealt with the addition of XLPE in chemically distinct polymer matrices, also encountered a decrease in tensile strength. Furthermore, the intensity of the drop tends to increase as the dispersed phase content increases, which may characterize high interfacial tension and poor adhesion between the phases, as highlighted by Hopewell et al.<sup>5</sup>. The poor adhesion between XLPE and PA12 was evidenced by SEM analysis as shown previously.

For the PA12/PE-g-MA5 formulation, which was made to assess the effect of the compatibilizer alone on PA12, a reduction in tensile strength of 9% was observed in comparison with the extruded PA12.

When PE-g-MA is added as a compatibilizer, a partial recovery of the tensile properties can be noted, being 4 wt% apparently the concentration with the greatest compatibilization effect, reaching a 16% increase compared to the result obtained for the non-compatibilized compound. This result corroborates the SEM analysis for the PE-g-MA4 formulation, in which a smaller number of gaps and holes are observed compared to the non-compatibilized compound. Considering the reduction observed in tensile strength when only PE-g-MA is added, the increase observed in the PE-g-MA2 and PE-g-MA4 formulations suggest an improvement in adhesion between the matrix and dispersed phase. By increasing the PE-g-MA content to 8 wt%, there is a slight reduction in tensile strength, returning to the levels found for 2 wt% compatibilizer. It is possible that part of the PE-g-MA has started to act as a third phase, and not just as a compatibilizer, generating a reduction in this property similar to that observed in the PA12/PE-g-MA5 formulation.

The results of strain at break and respective standard deviations are presented in Figure 10. A significant reduction in the strain at break of the extruded PA12 is seen compared to the PA12 that did not undergo extrusion. This reduction in strain at break may be attributed to an increase in the degree of crystallinity after the extrusion process, as shown by the DSC results. The incorporation of XLPE into the PA12 matrix reduced the strain at break by 88%. According to Utracki and Wilkie<sup>38</sup>, the drastic reduction of this property when adding a dispersed phase may indicate poor adhesion between phases, as evidenced by SEM analyses. This result was already expected, since PA12 and XLPE are chemically not very similar, thus requiring the presence of a compatibilizer.

The addition of PE-g-MA had a great effect on the partial recovery of strain at break; recovery increased with increasing compatibilizer. For the 8 wt% PE-g-MA, an increase of 180% in elongation was found compared to the formulation without compatibilizer. As the result obtained



Figure 10. Bar graph of strain at break of PA12 and its different compounds.

for the PA12/PE-g-MA5 formulation shows that the addition of PE-g-MA to PA12 reduces elongation, the observed increases in this property in the PE-g-MA2, PE-g-MA4, and PE-g-MA8 suggests that some compatibilization of the compound occurred, evidenced by the SEM results for this formulation.

Figure 11 shows the results obtained for the tensile modulus. The formulation referring to the extruded PA12 showed an increase of approximately 30% compared to the PA12 that did not undergo extrusion. As previously mentioned, this increase is probably related to the increase in the degree of crystallinity of PA12 after the extrusion process.

It can be seen that the addition of 20 wt% XLPE in the PA12 matrix resulted in a decrease of approximately 40% in the tensile modulus compared to the neat PA12 that underwent the same extrusion process. A reduction in stiffness was already expected because the flexibility of XLPE is greater than the flexibility of PA12.

The addition of 2 wt% PE-g-MA to XLPE maintained this property. Increasing the compatibilizer concentration to 4 and 8 wt% resulted in a drop of approximately 30% in stiffness compared to composition 4 (without compatibilizer). This can be explained by the result obtained in the PA12/ PEgMA5 composition, which shows that the addition of 5 wt% PE-g-MA strongly reduces PA12 stiffness. These results suggest that after a certain concentration, the compatibilizer starts to assume the role of a third phase of the compound, significantly modifying its mechanical properties. As polyethylene has a lower tensile modulus than PA12, the effect was a reduction in stiffness.

## 3.6.2. Impact testing

The mean values found in the impact test and their respective standard deviations are shown in Figure 12.

The extruded PA12 showed a lower impact strength compared to the non-extruded PA12, as expected due to the increase in the degree of crystallinity mentioned in the previous results. Thus, the increase in the degree of crystallinity of the extruded PA12 in relation to the non-extruded one resulted in an increase in both tensile strength and elastic modulus,



Figure 11. Bar graph of tensile modulus of PA12 and its different compounds.



Figure 12. Bar graph of impact strength of PA12 and its different compounds.

and a reduction in both the strain at break and the impact strength, as expected.

Incorporation of XLPE waste into the PA12 matrix resulted in a 120% increase in impact strength. This result was already expected due to the rubbery nature of XLPE, since its reticulated structure favors the absorption of mechanical energy. This result corroborates the results found for the tensile modulus, which showed that the addition of XLPE increases the flexibility of PA12. Lindqvist et al.<sup>12</sup> and Silva<sup>13</sup> also found significant increases in impact strength when incorporating XLPE into a polypropylene matrix.

When 2 wt% PE-g-MA was added, a decrease in impact strength was noted in relation to the non-compatibilized compound. As already seen in the tensile modulus results, when compatibilizer content increases from 4 and 8 wt% the compound gains flexibility, and thus the impact strength will increase, stabilizing close to the value obtained in the PA12/ PEgMA5 composition, which refers to the incorporation of only PE-g-MA in PA12.

### 3.6.3. Flexural testing

The results obtained for flexural modulus and strength are shown in Figures 13 and 14, respectively.

Corroborating once again the assumption of an increase in the degree of crystallinity when PA12 is extruded, an increase in the flexural modulus is observed in the PA12-EXT formulation compared to the non-extruded PA12 formulation.

The addition of 20 wt% XLPE waste reduces the flexural modulus by approximately 27%. The decrease in this property was expected since XLPE has a more flexible and rubbery



Figure 13. Bar graph of flexural modulus of PA12 and its different compounds.



Figure 14. Bar graph of flexural strength of PA12 and its different compounds.

behavior compared to PA12. This reduction in the flexural modulus was also found in the works by Silva<sup>13</sup> and Soares<sup>34</sup>, who added XLPE in PP and PA6 matrixes, respectively. They also found that this property tends to reduce more with increasing XLPE content.

The addition of 2 wt% PE-g-MA did not have a significant effect on the flexural modulus. The increase in the compatibilizer content resulted in a reduction in the flexural modulus value. This result suggests that the addition of PE-g-MA rendered the compound more flexible, as expected.

As expected, the results for flexural strength follow the same trend as the results previously presented for flexural modulus. After the incorporation of XLPE waste, a reduction of approximately 31% in flexural strength compared to neat PA12 was noticed. With the incorporation of PE-g-MA, the results are similar to those obtained for the flexural modulus.

## 4. Conclusions

PA12 compounds containing 20 wt% XLPE waste, without or with PE-g-MA at 2, 4, and 8 wt%, were successfully prepared in a corotating twin-screw extruder, with subsequent injection molding of test specimens.

As expected by the different chemical structures, the SEM tests showed a lack of adhesion between the PA12 matrix and the XLPE dispersed phase, characterized by the gaps between the two phases. Adding PE-g-MA improves compatibility, and the micrographs showed fewer gaps and a more regular surface.

The HDT tests showed that for PA12, the addition of the cross-linked polymer reduces its ability to sustain a load at high temperatures. The effect is slightly aggravated with the addition of the compatibilizer.

The DSC tests showed a reduction in the degree of crystallinity of PA12 with the addition of cross-linked polyethylene, with an even greater reduction when the compatibilizer was added. The addition of both XLPE and compatibilizer had little effect on DSC melt and crystallization temperatures.

The mechanical tests corroborated the analyses carried out in SEM. The addition of XLPE in the PA12 thermoplastic matrix caused a drastic reduction in most of the properties studied, except for impact strength, which increased by 120%. The addition of PE-g-MA as a compatibilizer proved to be efficient in partially recovering properties such as tensile strength and strain at break, with the possibility of enhancing the increase in impact strength observed in the formulation without compatibilizer.

Hence, using XLPE waste in a PA12 matrix can be a feasible alternative for applications in which impact strength is important. Moreover, adding XLPE should promote a significant cost reduction in the final product, as it uses industrial waste that is substantially less expensive than PA12. The formulation containing 4 wt% PE-g-MA proved to be the most interesting, combining good recovery of mechanical properties, greater increase in impact strength, and medium content application of compatibilizer.

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