

Quantitative Effects of Ecuadorian Silicon-Aluminum Materials on the Degradation Rate and Mechanical Strength Enhancement of Recycled Polyethylene

Edward H. Jiménez^{1*}, Gabriela Mejía¹, Marlon Cuenca², Belén Granja², Javier Fuentes², Patricia Ochoa¹, Gustavo López¹, José Bermudez¹, Fernando García¹, Sandra Gavilanes¹, Washington Ruiz¹ and Alexis Martial Debut³

¹Universidad Central del Ecuador, Facultad de Ingeniería Química, Ciudad Universitaria, Ritter s/n & Bolivia, Quito, Ecuador.

²Universidad Central del Ecuador, Facultad de Arquitectura y Urbanismo.

³Universidad de las Fuerzas Armadas ESPE, Head of the Nanomaterials Characterization Laboratory, Sangolquí Ecuador

Corresponding author: Edward Jiménez, Researcher (Chemical Engineering), Universidad Central del Ecuador, Quito, Ecuador

Received: June 3, 2024 Accepted: October 5, 2024 Online Published: October 30, 2024

doi:10.5539/jmr.v16n5p31

URL: <https://doi.org/10.5539/jmr.v16n5p31>

Abstract

This study presents an innovation in the use of a native Ecuadorian nanoporous material known as allophane for the reprocessing of greenhouse plastics to obtain a functional polymer that allows for reuse, improving its mechanical properties and/or increasing its lifespan. By achieving this objective, three problems are simultaneously addressed: 1) the need to recycle used plastics in a prominent Ecuadorian flower company committed to environmental preservation, 2) the scientific viability work carried out by the Central University of Ecuador, and 3) the industrial application of recycled plastics and pellet production.

Blown film extrusion was used to prepare low-density polyethylene sheets with different amounts of Ecuadorian allophane microparticles (30 ± 5 micrometers) (0.1%, 0.3%, and 0.5% by weight). Mechanical property studies were conducted following ASTM D 882 standards, and thermal stability was characterized using thermogravimetry.

The results showed an increase in elongation at break and Young's modulus percentages as the concentration of the additive increased, demonstrating its physical-chemical compatibility. Additionally, the effect on the polymer's thermal degradation was analyzed, resulting in a directly proportional relationship between activation energy and the concentration of the material. Finally, these results demonstrate that allophane as an additive enhances the mechanical properties of recycled low-density polyethylene (12-36%) and accelerates its thermal degradation process, reducing environmental impact.

Keywords: Allophane, Plastic recycling, mechanical properties, Thermal degradation

1. Introduction

In the floriculture industry, low-density polyethylene (LDPE) is extensively utilized for greenhouse construction, requiring approximately 2000 kg per hectare, as reported by Gudiño (2011). This material is replaced cyclically every three years, resulting in a substantial volume of plastic waste that presents significant environmental and economic challenges. Given this situation, traditional waste management methods, such as landfilling and incineration, are increasingly scrutinized due to international policies emphasizing efficient material and energy recovery. Therefore, there is an urgent need to develop innovative recycling strategies to mitigate these environmental impacts.

In this context, exploring advanced technologies that can enhance the properties of recycled plastics becomes crucial. One promising approach is the use of specialized additives that improve the performance of recycled materials. Recent studies have demonstrated that incorporating layered silicates into polymers can significantly enhance their mechanical properties, increase flame retardance, and improve thermal resistance (Fu and Naguib, 2006; Yoseidaegil, 2015). The effectiveness of these fillers is influenced by factors such as size, aspect ratio, hybrid morphology, and dispersion quality. Thus, leveraging these advanced additive technologies offers a viable pathway to improve the properties of recycled LDPE, thereby extending its functional lifespan and enhancing its usability.

Building on this approach, Jimenez (2018) examined the properties of Ecuadorian allophane, an amorphous mineraloid composed of aluminum silicate with a low organic carbon content and a Si/Al ratio between 1.3 and 1.4. Allophane's applications include phosphate and water retention, CO₂ adsorption, and use as a fertilizer additive. Additionally, recent research by Espinoza (2019) further supports its potential in enhancing the stability and resistance of asphalt and concrete. These findings suggest that allophane could serve as an effective reinforcement and additive for polymeric materials, making it a promising candidate for improving recycled plastics.

This study aims to investigate the potential of Ecuadorian allophane as an additive to enhance the mechanical and thermal properties of recycled LDPE composites. Various LDPE films with added allophane were evaluated to assess their impact on material properties such as elastic modulus, tensile strength, and elongation at break. Additionally, the kinetic parameters of thermal decomposition were analyzed using the isoconversional model of Friedman. The insights gained from this research will inform the design of composite materials incorporating recycled plastics and allophane, improving their mechanical properties and contributing to more sustainable waste management practices in the agricultural industry. Furthermore, these advancements also open opportunities for secondary applications, such as trash bags, by enhancing the durability and functional performance of the recycled material.

2. Materials and Methods

2.1 Materials

The study employed low-density polyethylene (LDPE) as the primary material, with its general properties and functions are detailed in Table 1. LDPE was donated by the floriculture company "Hoja Verde," located in Cayambe, Ecuador, where it had been used as a greenhouse cover for approximately three years. The pure allophane, utilized as an additive in this research, was extracted from Santo Domingo de los Tsáchilas, Ecuador, with approximate coordinates of -0.1386 latitude and -79.078 longitude.

Table 1. Materials and their function used in the study

Material	Properties	Function
LDPE	Elongation at break	Matrix
	MD: 383 %	Ease of processing
	TD: 575%	
	Tensile strength	
	MD: 149 MPa	
	TD: 154 MPa	
	Yield strength	
Allophane	MD: 102 MPa	
	TD: 100 MPa	
	Ease of processing	Dispersed phase
	Particle size 19-30 µm	Reinforcement

2.2 Reprocessing

Reprocessing was conducted using a Covex single-screw extruder equipped with a 30 hp motor, operating at a screw speed of 80 rpm. The extruder's temperature profile was meticulously controlled across seven distinct zones, ranging from 120 to 190 °C. LDPE-allophane composite films were produced by melt-extruding the material to incorporate allophane at loadings of 0.1, 0.3, and 0.5 wt%. Prior to extrusion, both LDPE and allophane particles were dried in an oven at 60 °C for 24 hours. Subsequently, the dried LDPE and allophane were combined in a blender before being fed into the extruder. The resulting films had a thickness of approximately 1 mm, facilitating a comprehensive assessment of their mechanical and physical properties

2.3 Characterization

2.3.1 Properties of allophane

BET Surface Area Analysis

The BET (Brunauer-Emmett-Teller) surface area analysis is a technique used to determine the specific surface area of a material through the adsorption of an inert gas on its surface. In the mentioned study, pure allophane was evaluated using a MICROMETICS Chemisorption Analyzer by N₂ impregnation to determine its specific surface area. Improving the specific surface area of plastic additives can increase the filling capacity, improve thermal stability, and enhance the mechanical strength of the material. (Mao et al., 2020)

Chemisorption

Chemisorption involves the adsorption of a gas onto a surface through a chemical reaction. The MICROMETICS Chemisorption Analyzer was used to quantify the active sites present in allophane by chemical adsorption with ammonia. Particle size was measured using a Thomas Scientific 1230CM optical microscope. Increased chemisorption allows for interaction of the material with the polymer matrix, thereby improving adhesion and mechanical strength of the composite material.

2.3.2 Greenhouse Plastic

Morphology

A Tescan Mira 3 scanning electron microscope (SEM) was used to investigate changes in the morphology of the film before and after incorporating the additive. SEM micrographs were taken at 15 kV and a working distance (WD) of 24 mm. Additionally, energy-dispersive spectroscopy (EDS) was used to analyze the elemental composition of the sample. In summary, the test demonstrates the adherence of allophane to LDPE films.

FTIR

In this study, a Perkin Elmer Spectrum Two FTIR instrument with attenuated total reflection (ATR) accessory was used to analyze the additives present in a polymer. The measurement range of 600 to 4000 cm⁻¹ allowed for the identification of functional groups in the sample, which is essential for understanding the chemical structure of the materials and the interactions between the components of the additive.

TGA

Thermogravimetric analysis made it possible to study the thermal stability of the polymer and obtain kinetic parameters that allowed understanding of its thermal degradation. Thermogravimetric tests were performed on a METTLER TOLEDO TGA STAR System, following the parameters described in ASTM E1131-20 (2020) for polyethylene, which includes an initial temperature of 26 °C, final temperature of 600 °C at a heating rate of 10 °C/min and N₂ atmosphere with a flow rate of 50 ml/min.

3. Results and Discussion

3.1 Properties of Allophane

The results presented in Table 2 provide quantitative insights into the characteristics of allophane particles prepared using various mesh sizes. The chemisorption measurements, expressed in cm³/g, reveal a narrow range of values, with a slight variation from 85.828 cm³/g for the smallest particles (45 μm) to 88.604 cm³/g for the intermediate particles (106 μm). This minimal variation in chemisorption values suggests a consistent availability of active sites across the different particle sizes, indicating a uniform potential for chemical interaction with the polymer matrix. The data imply that the adhesive properties of the allophane, in terms of chemisorption, are relatively independent of particle size.

The BET surface area data, expressed in m²/g, exhibit a marked correlation with particle size. The intermediate particles, characterized by mesh No. 140, achieved the highest BET surface area of 81.537 m²/g. This represents a significant increase in specific surface area compared to the smallest particles (46.614 m²/g) and the largest particles (45.006 m²/g). The pronounced elevation in BET surface area for the intermediate-sized particles indicates a greater available surface area for interaction with the polymer matrix. This increased surface area facilitates more effective dispersion and integration of the additive within the composite material, as highlighted by Lee, D. W., & Yoo, B. R. (2016) in their study.

Quantitatively, the BET surface area for the particles with a mean size of 30.915 μm (mesh No. 140) is approximately 75% higher than that for the smallest particles and nearly double that for the largest particles. This indicates a critical size range where the surface area is maximized, potentially leading to improved mechanical and thermal properties of the composite due to better distribution and interaction of the additive.

Table 2. Characterization

Mesh Size No.	325	140	40
Physical Separation	45 [μm]	106 [μm]	425 [μm]
Chemisorption [cm^3/g]	85,828	88,604	87,885
BET [m^2/g]	46,614	81,537	45,006
Particle [μm]	$\mu= 17,817$ N=7000	$\mu= 30,915$ N=5400	$\mu= 81,877$ N=3400

Note: Table 2 shows the characterization of allophane evaluating three particle sizes obtained by sieves governed by the ASTM-E-11 standard. Where N represents the population size, and μ is the particle size mean particle size expressed in micrometers [μm]. The mean was obtained by measuring the length of each particle shown in Figure1 using ImageJ software.

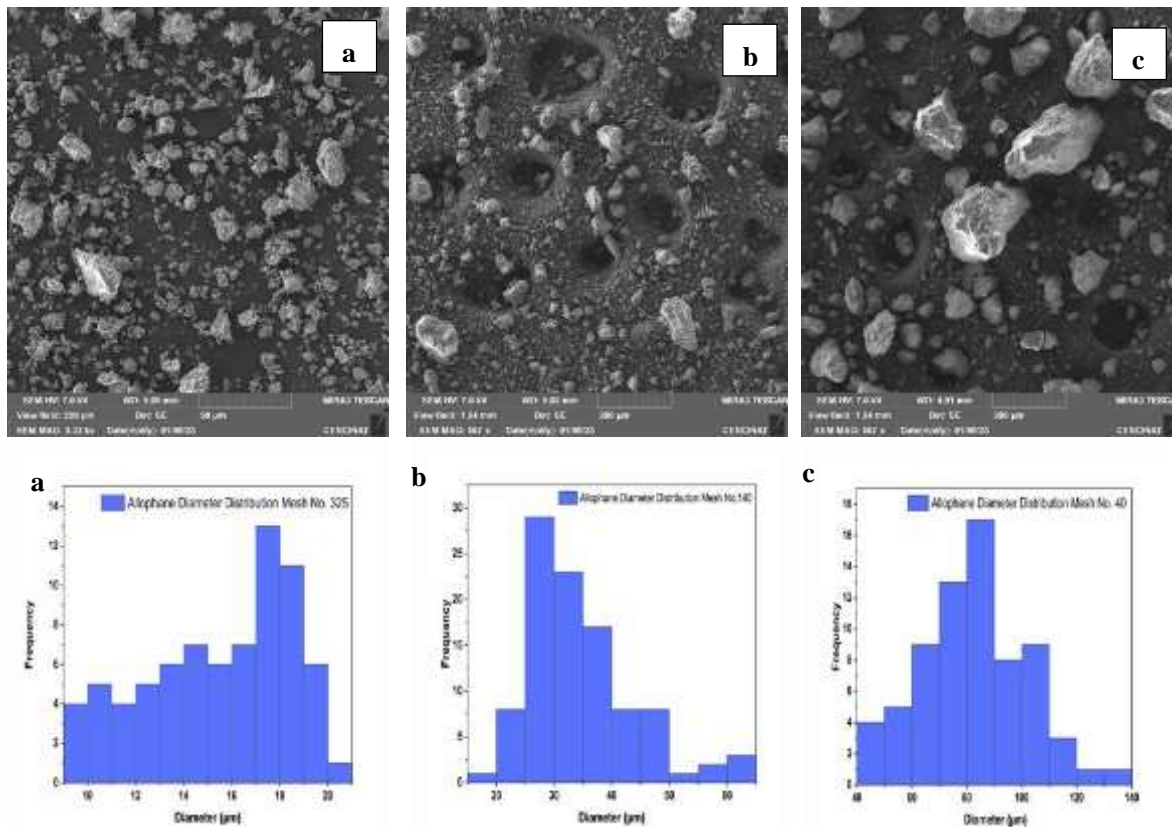


Figure 1 Shows the distribution of allophane particles, and their morphology captured by Tescan Mira 3 scanning electron microscope (SEM). (a) Distribution for mesh size #325, (b) distribution for mesh size #140 and (c) distribution for mesh size #40

The analysis of the particle size distribution, characterized by the mean particle size (μ) and the number of particles (N), shows that the intermediate-sized particles ($\mu = 30.915 \mu\text{m}$, $N = 5400$) achieve an optimal balance between surface area and particle size. The smaller particles ($\mu = 17.817 \mu\text{m}$, $N = 7000$) and the larger particles ($\mu = 81.877 \mu\text{m}$, $N = 3400$) offer lower surface areas, which could limit their effectiveness in reinforcing the composite material and thermal stability of the

composite material.

3.2 Appearance of Plastic Bags

The appearance of blown LDPE films with and without additive is shown in Figure 2. The inclusion of allophane micro-particles in different proportions has been shown to improve the appearance of the films by reducing and preventing the formation of gels in their structure. This improvement is due to the hygroscopic and adsorption properties of the additive, which allows it to absorb the moisture present in the plastic material and/or the presence of air or gases during the extrusion process. Consequently, the characteristics of the additive favor the elimination of bubbles or surface defects in the film, resulting in a more homogeneous and better-looking film. The opacity of the films as the additive increases is affected due to the color of allophane (brownish-yellow).

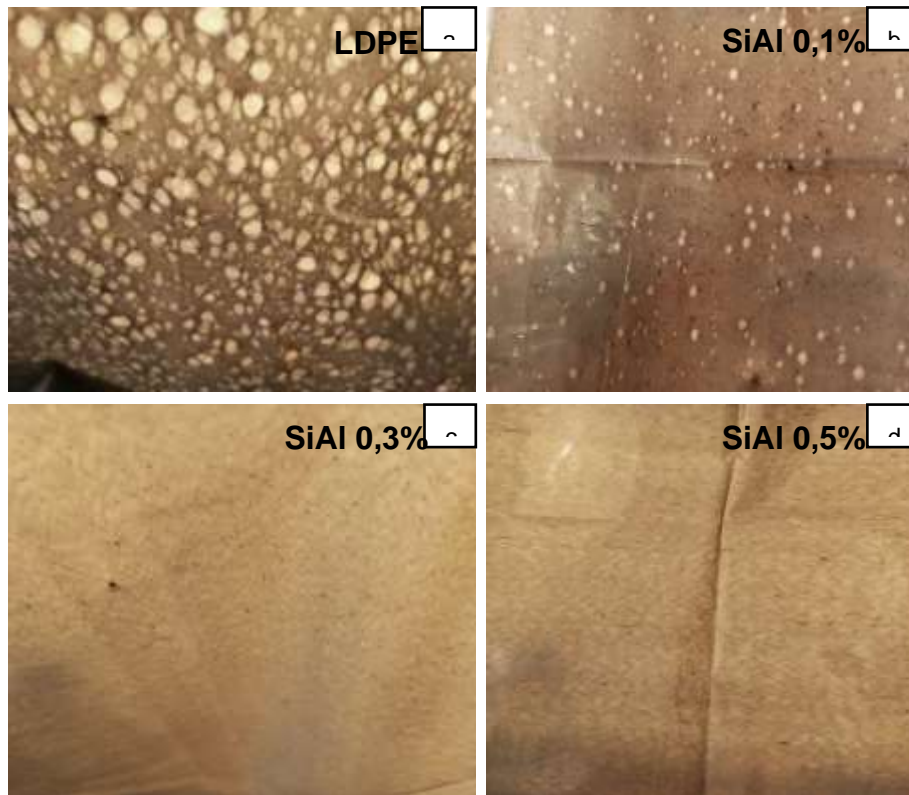


Figure 2. Appearance of the films reprocessed with and without additive, in their application for garbage bags. (a) LDPE without allophane, (b) LDPE with 0,1wt% of allophane, (c) LDPE with 0,3wt% of allophane and (d) with 0,5wt% of allophane

3.3 Allophane in Plastic Bags

Scanning Electron Microscopy (SEM) was employed to investigate the interaction between the LDPE film and the allophane additive. As shown in Figure 3, the presence of allophane significantly affects the morphology of the films, with micrometer-sized particles becoming increasingly apparent on the surface of the polymer matrix at higher additive concentrations of 0.1wt%, 0.3wt%, and 0.5wt% by weight. This increase in particle density suggests effective adhesion of allophane to the LDPE films. These findings align with previous studies demonstrating that the dispersion of additives in polymer matrices can alter the material's surface structure (Bumbudsanpharoke & Ko, 2015). Specifically, Bumbudsanpharoke and Ko (2015) observed that higher nanoclay loading in LDPE led to the formation of micro-void structures, consistent with the segregation and dispersion of additives within the polymer matrix. Additionally, Mazzanti et al. (2020) reported the presence of multilayered structures at higher additive concentrations, indicating a complex interaction between the additive and the LDPE matrix. This study underscores the need for effective homogenization between the matrix and allophane to enhance material uniformity and mechanical properties. Although the compatibility between allophane and LDPE is evident, further optimization is required to achieve a more homogeneous dispersion, thereby improving the material's mechanical performance. These results highlight the importance of adjusting additive concentration and mixing processes to maximize the benefits of allophane in enhancing the properties of recycled LDPE.

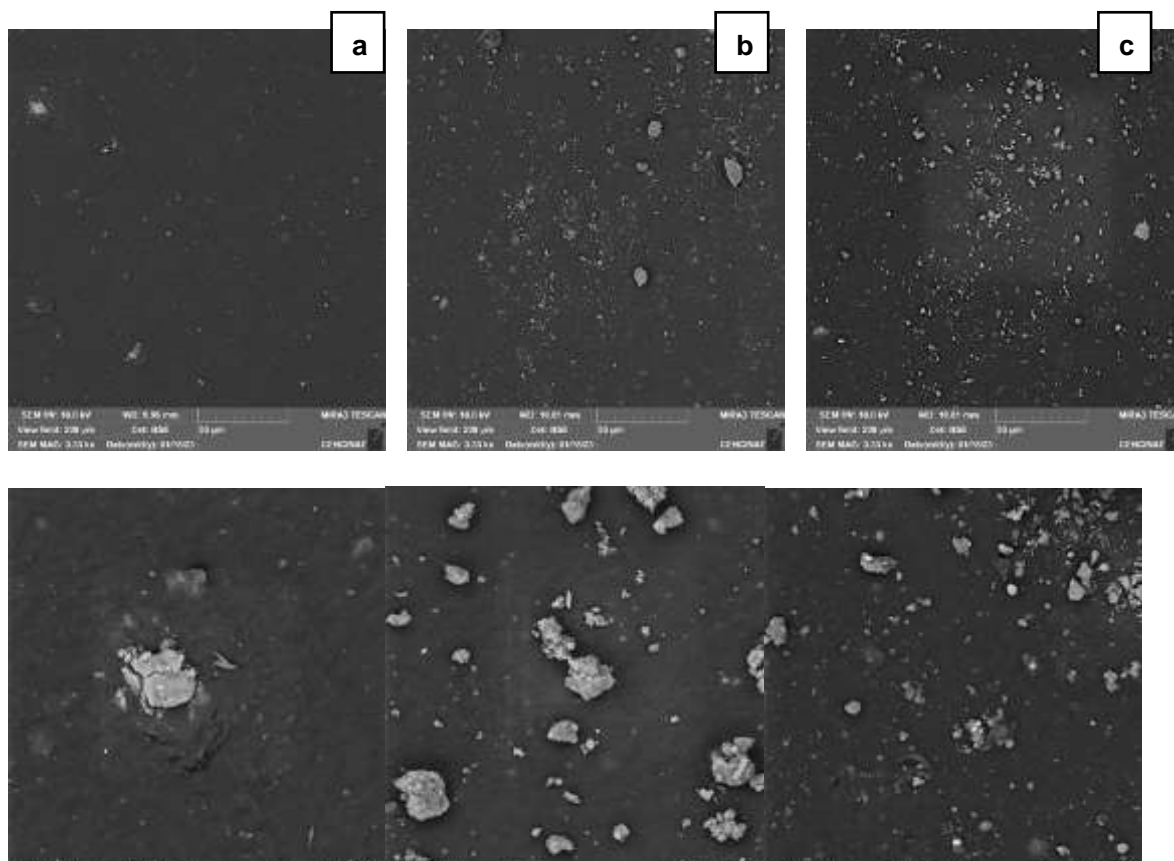


Figure 3. SEM photographs show the inclusions of allophane in the matrix of the reprocessed LDPE. They are observed at two scales, 50 and 10 μm. a) Corresponds to LDPE with a concentration of 0.1% SiAl, b) LDPE with a concentration of 0.3% SiAl and c) LDPE with a concentration of 0.5% SiAl

Figure 4 of the study demonstrates that through energy-dispersive X-ray spectroscopy (EDS) analysis, the presence of allophane particles on the surface of the polymeric material can be identified. This result suggests the additive is able to adapt to the interface of the polymeric matrix. In addition, a comparison was made between the elemental composition of carbon (C) and allophane (Si/Al) in the material, where micro-holes can be observed as a product of the degradation of the recycled material, which are reinforced by the additive.

3.4 FTIR-ATR Analysis

Figure 5 shows the superposition of spectra using allophane as an additive at different concentrations. The peaks corresponding to the aliphatic functional group (-CH₂-CH₂)_n are observed, confirming that low-density polyethylene is being analyzed. These peaks are located between 3000 and 2800 cm⁻¹, with two bands of medium intensity, one between 1500-1400 cm⁻¹ and the other between 800-700 cm⁻¹. It is important to highlight the presence of the peak at 1737 cm⁻¹, as it may indicate material degradation as it falls within the range established for carbonyl groups.

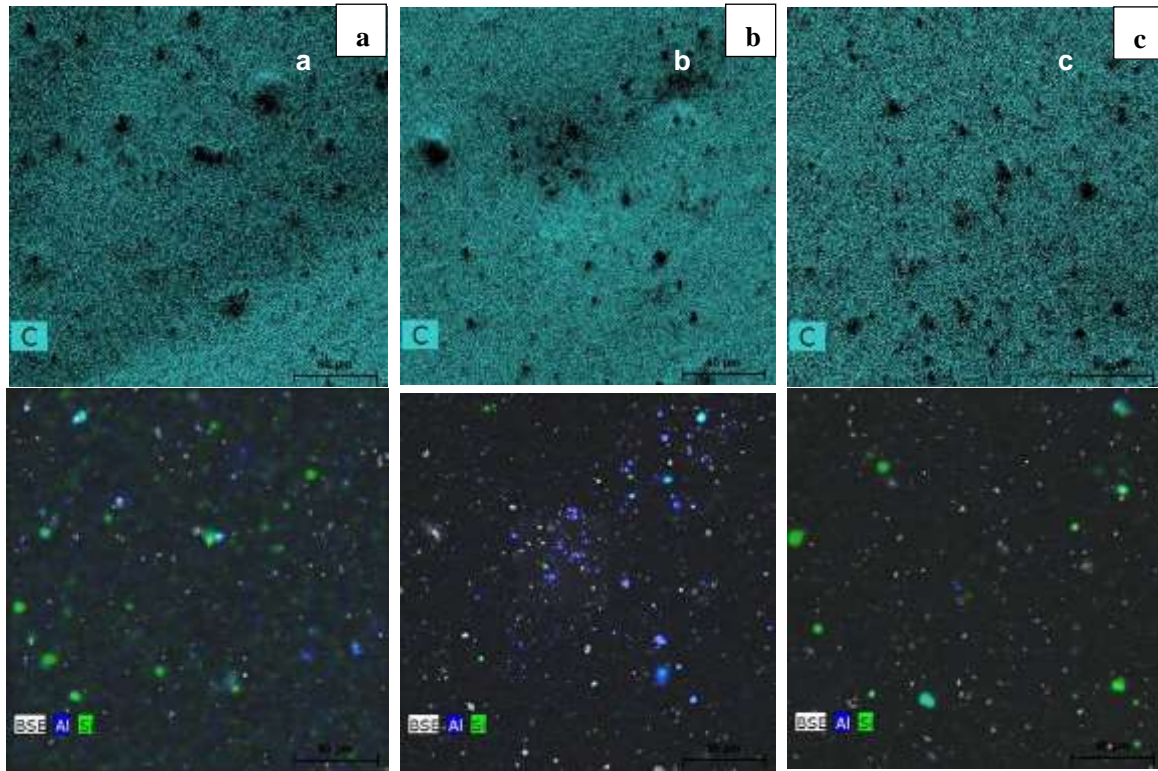


Figure 4. shows SEM-EDS micrographs that demonstrate the presence of allophane in reprocessed films, observed at 50 [μm]. a) Corresponds to LDPE with a concentration of 0.1% SiAl, b) LDPE with a concentration of 0.3% SiAl and c) LDPE with a concentration of 0.5% SiAl

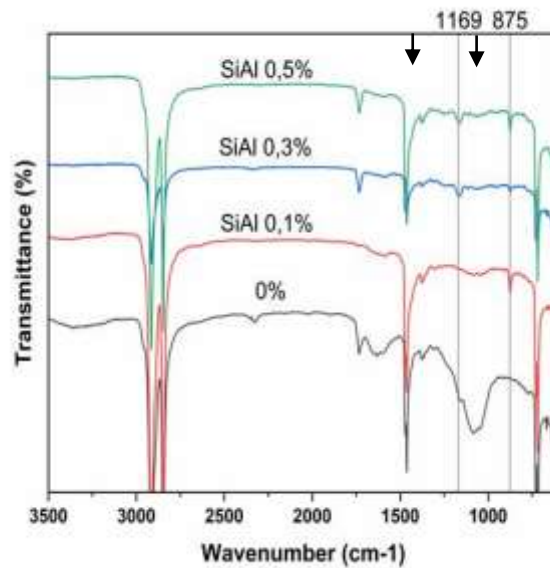


Figure 5. shows the IR spectrum of the polyethylene reprocessed with aluminosilicate at different concentrations. Studies on aluminosilicate by Bravo et al. (2013) and Papadakis et al. (2000) suggest the presence of characteristic bands between 560-1640 cm^{-1} , which correspond to various vibrational modes of the aluminosilicate structure. Additionally, they note that wavenumbers ranging from 1640-3500 cm^{-1} are associated with the stretching and bending of hydroxyl groups, indicative of water in amorphous materials. This hygroscopic nature is further corroborated by Jiménez's findings

(2013). The presence of bands between 1100-1300 cm^{-1} also indicates the existence of SiO_4^{4-} , a key component of the aluminosilicate material.

Although the characteristic bands of aluminosilicate were not distinctly observed in the FTIR spectrum of the composites, it is inferred that the bonding with polyethylene is facilitated by Van der Waals forces, which act between non-polar molecules. This inference is supported by SEM and EDS analyses (Figures 3 and 4), where the presence of aluminosilicate particles on the surface of the plastic material was confirmed. These results suggest that the interaction between polyethylene and aluminosilicate involves Van der Waals forces, indicating effective compatibility and the potential for aluminosilicate to act as a reinforcing agent.

In accordance with these findings, the FTIR spectra of clay, as reported by Zazoum et al. (2013), exhibit distinct absorption peaks at approximately 521 and 1047 cm^{-1} ; characteristic of silica (Si) and aluminum (Al). These peaks are attributed to the stretching and bending modes of these elements. This observation further supports the hypothesis that similar inorganic additives, such as aluminosilicate, may also exhibit increased spectral presence and a reinforcing effect within the polymer matrix.

3.5 Thermal Degradation

The thermal degradation of a polymer is typically assessed using thermogravimetric analysis (TGA), which measures the percentage of weight loss of the sample as a function of temperature. A key parameter is the onset temperature of degradation ($T_{10\%}$), defined as the point at which 10% of the sample's weight is lost. Table 3 and Figure 6 present the TGA weight loss profiles (%) against temperature. The results show that the thermal stability of LDPE modified with allophane is superior to that of neat LDPE. At $T_{10\%}$, the initial thermal degradation of the allophane-modified composites occurs at higher temperatures compared to neat LDPE (445 °C). The $T_{10\%}$ value increases with the addition of allophane, reaching a maximum of 456.6 °C at 0.5 wt.% Si/Al content. This trend is consistent with findings reported in other studies (Olewnik, Garman, & Czerwinski, 2010; Hemati & Garmabi, 2011). The improvement in thermal stability can be attributed to the formation of an insulating and incombustible carbonaceous-silicate layer on the surface of the composite during combustion. This layer acts as a barrier, preventing the escape or diffusion of low molecular weight volatile products within the composite and shielding the underlying polymer from the surrounding heat. Additionally, the physico-chemical adsorption of volatile decomposition products onto the silicates/allophane could delay the volatilization of products generated from carbon-carbon bond scission in the LDPE matrix.

To evaluate the kinetic parameters, Das & Tiwari (2017) state in their research that for the degradation of polymers, it is generally assumed that the conversion rates are proportional to the concentration of the reacting material. Therefore, the conversion rate can be expressed by the following basic kinetic equation:

$$\frac{d\alpha}{dt} = \beta \frac{d\alpha}{dT} = k(T)f(\alpha) \quad (1)$$

In this equation, the rate constant $k(T)$ and the conversion function $f(\alpha)$ depend on the temperature T and the degree of conversion α respectively. This approach quantitatively describes the thermal degradation of polymers and is crucial for interpreting data obtained from thermogravimetric analysis (TGA).

Where β is the heating rate and (α) is the conversion degree defined by:

$$\alpha = \frac{m_i - m_t}{m_i - m_f} \quad (2)$$

Where m_t is the mass at time t , and m_i , m_f are the initial and final masses, respectively. Refers to values at the beginning and the end of the weight loss event of interest.

The temperature dependence of the reaction rate constant $k(T)$, can be expressed in terms of the Arrhenius equation:

$$k(T) = Ae^{\left(\frac{Ea}{RT}\right)} \quad (3)$$

Where A is the pre-exponential factor (s^{-1}), Ea is the activation energy (kJ/mol), T is temperature in Kelvin and R is the gas constant (0.008314 $\text{kJmol}^{-1}\text{K}^{-1}$)

Combining equations (2) and (3) yields the reaction rate:

$$\beta \frac{d\alpha}{dT} = Ae^{\left(\frac{Ea}{RT}\right)} f(\alpha) \quad (4)$$

The differential model proposed by Friedman assumes the use of the logarithm of the conversion differential ($d\alpha/dT$) as a reciprocal function of temperature, obtaining:

$$\left(\frac{d\alpha}{dt}\right) = \ln\left(\beta \frac{d\alpha}{dT}\right) = \ln(A) - \frac{Ea}{RT} + \ln(f(\alpha)) \tag{5}$$

This method was selected for its capability to provide accurate kinetic parameters by assessing the activation energy at different levels of conversion, without assuming a specific reaction mechanism. The isoconversional method of Friedman involves analyzing TGA data at various stages of thermal degradation. By plotting the natural logarithm of the rate of mass loss against the inverse temperature, a linear relationship was derived, which is a standard approach in kinetic studies. The linear regression model facilitated the extraction of activation energy as a function of conversion degree with efficiency. Linear regression provides a straightforward method to quantify the relationship between activation energy and conversion degree. In this study, the model allowed for precise estimation of activation energy, fitting well with the experimental data obtained from TGA. The linear model ensures that the derived kinetic parameters are consistent and reliable for different concentrations of allophane.

The kinetic parameters corresponding to activation energy Ea and pre-exponential factor A are calculated from the slope and intercept resulting from the linear regression obtained by graphing $\ln(d\alpha/dT)$ vs $1/T$.

$$y = \ln\left(\frac{d\alpha}{dt}\right) \tag{6}$$

$$m = \frac{Ea}{R} \tag{7}$$

$$b = \ln(A) \tag{8}$$

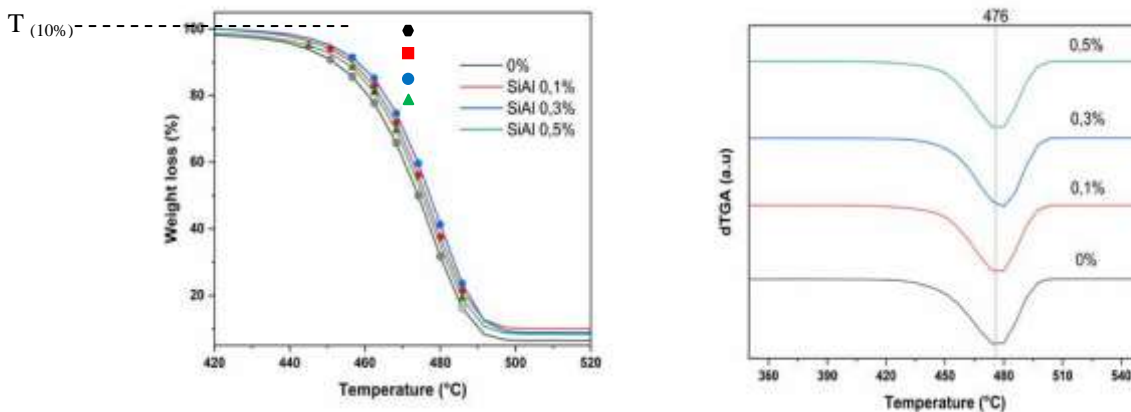


Figure 6 shows the results of the TGA and dTGA analysis for films with different concentrations of allophane

The quantitative analysis of thermal degradation for LDPE composites with varying concentrations of silicon-aluminum (Si/Al) allophane reveals significant insights into the material's thermal stability and degradation kinetics. The temperature at 10% weight loss increases with the addition of allophane, from 445 °C for pure LDPE to 456.6 °C for LDPE with 0.5 wt% Si/Al. This indicates an enhancement in thermal stability with higher allophane content. The kinetic parameters, derived from the Arrhenius plot, show a decrease in activation energy from 309.19 kJ/mol for pure LDPE to 216.00 kJ/mol for LDPE with 0.1 wt% Si/Al, suggesting a lower energy barrier for thermal degradation with initial allophane addition. However, at 0.3 wt% and 0.5 wt% Si/Al, the activation energy increases to 244.56 kJ/mol and 251.72 kJ/mol, respectively, reflecting improved stability at these concentrations. Additionally, the pre-exponential factor varies significantly, ranging from 1.84206E+19 s⁻¹ for pure LDPE to 1.12212E+15 s⁻¹ for LDPE with 0.5 wt% Si/Al, indicating changes in the rate of degradation. The correlation coefficients (R^2) for the linear regressions range from 0.86 to 0.93, demonstrating a good fit of the kinetic model to the experimental data and ensuring the reliability of the results. These findings suggest that allophane effectively enhances the thermal stability of LDPE composites, with optimal concentrations providing the best balance between reduced activation energy and improved degradation resistance.

Table 3 presents the kinetic parameters of decomposition for the additive LDPE

Sample	%	Temperature at 10% weight loss (°C)	Linear Regression	Ea kJ/mol	Factor s ⁻¹	R ²
LDPE	0	445,00	$\ln\left(\frac{d\alpha}{dt}\right) = -\frac{37190}{T} + 44,36$	309,19	1.84206E+19	0,93
	0,1	450,83	$\ln\left(\frac{d\alpha}{dt}\right) = -\frac{25981}{T} + 28,55$	216,00	2.50673E+12	0,86
LDPE + Si/Al	0,3	456,30	$\ln\left(\frac{d\alpha}{dt}\right) = -\frac{29416}{T} + 33,29$	244,56	2.86856E+14	0,88
	0,5	456,60	$\ln\left(\frac{d\alpha}{dt}\right) = -\frac{30277}{T} + 34,65$	251,72	1.12212E+15	0,87

3.6 Tensile-Deformation

The tensile test of film samples was carried out according to the ASTM D882 "Standard Test Method for Tensile Properties of Thin Plastic Sheeting" using an Instron 3365 universal testing machine. At least five rectangular film samples (15 x 200 mm) were tested in both the machine direction (MD) and transverse direction (TD). Samples with a gauge length of 36.3 mm were subjected to the tensile test using a 5 kN load cell and a head speed of 500 mm/min. The average values of the Young's modulus, tensile strength, and elongation at break were calculated and reported.

Table 4. Mechanical properties of the film

Sample	%	Direction	Elongation at Break (%)		Tensile Strength (MPa)		Young's modulus (MPa)	
LDPE	0%	MD	580	± 45,9	22,2	± 1,4	148	± 5,1
	0%	TD	650	± 47,7	18,8	± 1,7	148	± 5,1
	0,1	MD	560	± 42,2	26,4	± 2,2	157	± 10,5
	0,1	TD	740	± 54,1	20,9	± 1,1	175	± 12,6
LDPE + Si/Al	0,3	MD	680	± 30,8	19,8	± 1,1	143	± 7,8
	0,3	TD	690	± 18,4	15,2	± 0,1	154	± 8,4
	0,5	MD	640	± 22	24,9	± 1	151	± 7,5
	0,5	TD	810	± 50,1	25,6	± 1,8	163	± 22,5

The mechanical properties of the LDPE/allophane composite films, as shown in table 3, exhibit notable variations with different concentrations of the allophane additive. The base LDPE film, produced via blown film extrusion without additives, showed balanced properties in the machine direction (MD) and transverse direction (TD), with a modulus of approximately 148 MPa, elongation at break of 600%, and tensile strength of 20 MPa. The incorporation of 0.1% w/w allophane significantly improved the modulus to 157 MPa and tensile strength to 26.4 MPa in the MD, while reducing the elongation at break to 560%. Increasing the allophane concentration to 0.3% w/w resulted in a decrease in the modulus (143 MPa) and tensile strength (19.8 MPa) in the MD, while elongation at break increased to 680%. With 0.5% w/w allophane, the modulus, tensile strength, and elongation at break improved to 151 MPa, 24.9 MPa, and 640%, respectively.

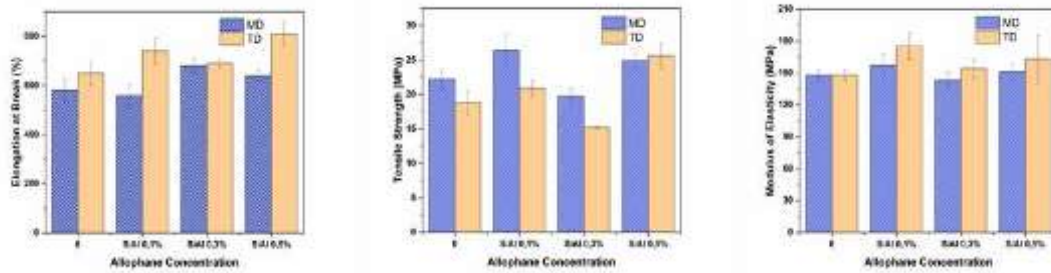


Figure 7. Elongation at break, tensile strength, and Young's modulus using allophane at different concentrations

These variations suggest a non-uniform distribution of allophane within the LDPE matrix, leading to inconsistent trends in mechanical properties. Despite this, the overall improvement in properties compared to the base sample indicates the potential benefits of allophane as an additive. The LDPE film with 0.5% w/w allophane showed the most significant improvements in elastic properties, aligning with the findings of Fu & Naguib (2006), who observed optimized mechanical responses in composite materials with 0.5% w/w montmorillonite nanoclay. Specifically, the LDPE films with 0.5% w/w allophane exhibited a 12% and 36% increase in tensile strength in the MD and TD, respectively, compared to the base plastic.

Interestingly, the values of Young's modulus were higher in the TD than in the MD, contrary to expectations based on the direction of bubble elevation during blown film extrusion. This suggests a potential reduction in crystallinity, as the allophane tends to remain amorphous. This distinctive behavior has been documented in studies of recycled films produced by blown film extrusion, such as those by Echeverria (2018) and Simpson & Harrison (2020), who attribute the dominance of the TD to polymer crystallization. The polymer crystals and the studied additive act as reinforcements, supporting the enhanced mechanical properties. Furthermore, Mazzanti et al. (2020) reported that similar behaviors were observed with other composite materials with TVP and PP matrix. The crystallinity reduction and the inherent characteristics of the matrix play significant roles in defining the overall mechanical performance.

4. Conclusions

The research demonstrates that incorporating Ecuadorian allophane into low-density polyethylene (LDPE) composites substantially enhances both their mechanical and thermal properties. Specifically, the addition of 0.5% (w/w) allophane results in a 12% increase in tensile strength in the machine direction (MD) and a remarkable 36% increase in the transverse direction (TD) compared to the base LDPE. Additionally, the Young's modulus improves with LDPE films exhibiting a 9% enhancement in MD and a 7% improvement in TD.

In terms of thermal stability, the study reveals that the activation energy for thermal degradation of LDPE composites rises with the addition of allophane. Notably, the activation energy for composites with 0.5% allophane is 15% higher than that of the base LDPE, signifying enhanced resistance to thermal degradation. This increase in activation energy aligns with the observed improvement in thermal stability, as higher allophane concentrations effectively elevate the energy barrier required for degradation processes.

The results highlight the importance of allophane particle size, with mesh No. 140 (approximately 106 microns) demonstrating optimal performance. This particle size not only maximizes the surface area available for interaction but also maintains effective chemisorption capabilities, leading to notable improvements in both mechanical strength and thermal stability.

These findings underscore the significant potential of allophane-enhanced LDPE composites for a range of advanced material applications. The enhancements observed in mechanical and thermal properties suggest these composites could be highly beneficial in sectors demanding materials with superior strength and stability. Future research should focus on exploring the practical applications of these composites in innovative technologies, particularly in the development of advanced materials that leverage their enhanced performance characteristics for demanding industrial applications.

5. Abbreviations

For better reader comprehension, the following abbreviations are identified:

- LDPE Low-Density Polyethylene
- SiAl Allophane
- MD Machine Direction

TD Transverse Direction

Funding: This work was supported by "Hoja Verde" Flowers Cia. Ltda.; and BIOIL-TECH Cia. Ltda.

References

- Aboulkas, A., El Harfi, K., & El Bouadili, A. (2010). Thermal degradation behaviors of polyethylene and polypropylene. Part I: Pyrolysis kinetics and mechanisms. *Energy Conversion and Management*, 51(7), 1363-1369. <https://doi.org/10.1016/j.enconman.2009.12.017>
- Allbrook, R. F. (1985). The effect of allophane on soil properties. *Applied Clay Science*, 1, 65-69. [https://doi.org/10.1016/0169-1317\(85\)90562-9](https://doi.org/10.1016/0169-1317(85)90562-9)
- Bravo, I., Montoya, J. C., & Menjivar, J. C. (2013). Retención y disponibilidad de fósforo asociado a la materia orgánica en un Typic Melanudands del departamento del Cauca, Colombia. *Acta Agronómica*, 62(3), 261-267.
- Bumbudsanpharoke, N., & Ko, S. (2015). A study of thermal properties of LDPE-nanoclay composite films. *Korean Journal of Packaging Science & Technology*, 21(3), 107-113. <https://doi.org/10.20909/kopast.2015.21.3.107>
- Das, P., & Tiwari, P. (2017). Thermal degradation kinetics of plastics and model selection. *Thermochimica Acta*, 654, 191-202. <https://doi.org/10.1016/j.tca.2017.06.001>
- Echeverría, T. (2020). *Caracterización de películas poliméricas multi-capas y viabilidad de su reciclado en forma de mezclas de alta performance* [Thesis]. UCE.
- Espinoza Yumi, T., & Valdivieso Ramírez, M. (2019). *Caracterización de mezclas asfálticas en caliente elaboradas con asfalto nano modificado con alofan puro* [Thesis]. UCE.
- Fu, J., & Naguib, H. E. (2006). Effect of nanoclay on the mechanical properties of PMMA/clay nanocomposite foams. *Journal of Cellular Plastics*, 42(4), 325-342. <https://doi.org/10.1177/0021955X06063517>
- Gudiño Predoiu, R. (2011). *Materiales Compuestos de Polietileno Reciclado con Partículas Lignocelulósicas (Aserrín)* [Bachelor Thesis]. QUITO/EPN.
- Hemati, F., & Garmabi, H. (2011). Compatibilised LDPE/LLDPE/nanoclay nanocomposites: I. structural, mechanical, and thermal properties. *The Canadian Journal of Chemical Engineering*, 89(1), 187-196. <https://doi.org/10.1002/cjce.941>
- Jiménez Calderón, E. H., Paucar Tipantuña, A. E., Herrera Mullo, P. F., Hidalgo Cháñez, D. A., Ruiz, W., Stahl, U., & Bermudez, J. (2020). Natural and activated allophane catalytic activity based on the microactivity test in ASTM norm 3907/D3907M-2019. *Applied Sciences*, 10(9), 3035. <https://doi.org/10.3390/app10093035>
- Jiménez, E. (2018). *Fisicoquímica de los Alofanos y sus Aplicaciones en Refinación de Crudo*. Universitaria.
- Jiménez, E. H., Paucar Tipantuña, A. E., Herrera Mullo, P. F., Hidalgo Cháñez, D. A., Ruiz, W., Stahl, U., & Bermudez, J. (2019). Nanotechnological characterization of allofanite and faujasite (Y-faujasite) catalysts and comparing with a commercial FCC catalyst (X-zeolite). *AIMS Materials Science*, 6(6), 911-943. <https://doi.org/10.3934/mat.2019.6.911>
- Kazemi, N. S. (2013). Use of recycled plastics in wood plastic composites—a review. *Waste Management*, 33, 1898-1905. <https://doi.org/10.1016/j.wasman.2013.05.017>
- Lee, D. W., & Yoo, B. R. (2016). Advanced silica/polymer composites: materials and applications. *Journal of Industrial and Engineering Chemistry*, 38, 1-12. <https://doi.org/10.1016/j.jiec.2016.04.016>
- Li, Q., Fu, Y., Zhang, R., Xu, M., & Zhao, X. (2015). Preparation and characterization of carbon nanotube/thermoplastic polyurethane composite fibers with improved mechanical and thermal properties. *Applied Surface Science*, 346, 339-346. <https://doi.org/10.1016/j.apsusc.2015.04.120>
- Mao, L., Chen, Y., Hu, J., Chen, Z., & Zhou, X. (2020). Effects of silica nanoparticles with different specific surface areas on the mechanical and thermal properties of silicone rubber composites. *Polymer Testing*, 87, 106500. <https://doi.org/10.1016/j.polymertesting.2020.106500>
- Mazzanti, V., Malagutti, L., Santoni, A., Sbardella, F., Calzolari, A., Sarasini, F., & Mollica, F. (2020). Correlation between mechanical properties and processing conditions in rubber-toughened wood polymer composites. *Polymers*, 12(5), 1170. <https://doi.org/10.3390/polym12051170>
- Mejía Rivas, G. E. (2022). *Uso de Nanomateriales como Aditivos en el Procesamiento de Plástico de Invernadero* [Thesis]. UCE.
- Olewnik, E., Garman, K., & Czerwinski, W. (2010). Thermal properties of new composites based on nanoclay,

- polyethylene and polypropylene. *Journal of Thermal Analysis and Calorimetry*, 101, 323-329. <https://doi.org/10.1007/s10973-009-0165-7>
- Papadakis, G., Briassoulis, D., Scarascia Mugnozza, G., Vox, G., Feuilleley, P., & Stoffers, J. A. (2000). Radiometric and thermal properties of, and testing methods for, greenhouse covering materials. *Journal of Agricultural Engineering Research*, 77(1), 7-38. <https://doi.org/10.1006/jaer.2000.0525>,
- Pavia, D. L., Lampman, G. M., Kriz, G. S., & Vyvyan, J. A. (2014). *Introducción a la espectroscopía*. Cengage Learning.
- Pineda Vásquez, M. A. (2022). *Caracterización de los asfaltos modificados con alquitrón ecuatoriano* [Thesis]. UCE.
- Simpson, D. M., & Harrison, I. R. (1994). A study of the effects of processing parameters on the morphologies and tensile modulus of HDPE blown films: application of composite theories on a molecular level to characterize tensile modulus. *Journal of Plastic Film & Sheeting*, 10(4), 302-325. <https://doi.org/10.1177/875608799401000404>
- Terán, A. E. (2013). *Diseño de los Procesos de Reducción de Tamaño, Secado y Granceado de Residuos Plásticos provenientes de Invernaderos*. Centro de Investigaciones Aplicadas a Polímeros (CIAP).
- UCE. (2019). *Físico Química de los alofanos y sus aplicaciones en refinación de crudo*. Editorial Universitaria e Instituto de Investigación Geológico y Energético.
- Zazoum, B., David, E., & Ngô, A. (2013). LDPE/HDPE/clay nanocomposites: effects of compatibilizer on the structure and dielectric response. *Journal of Nanotechnology*, 2013, 1-11. <https://doi.org/10.1155/2013/243956>

Copyrights

Copyright for this article is retained by the author(s), with first publication rights granted to the journal.

This is an open-access article distributed under the terms and conditions of the Creative Commons Attribution license (<http://creativecommons.org/licenses/by/4.0/>).