HDPE/aramid laminates reinforced with MMT20A for ballistic protection

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Abstract – With recent advances in weaponry, the demand for lightweight, strong, and efficient materials for ballistic protection has increased. Ballistic barriers play an essential role in safeguarding users in conflict zones, requiring structures with high mechanical performance, energy dissipation capacity, and flexibility. In this context, laminated composites of aramid fabric and polymer films emerge as promising alternatives. This study aims to evaluate the mechanical and thermal properties of multilayer panels consisting of aramid fabric and high-density polyethylene (HDPE) films modified with different concentrations of Cloisite 20A montmorillonite clay (MMT20A). HDPE films containing 1.0%, 2.5%, 5.0%, and 7.5% (wt.%) by weight of MMT20A were produced by extrusion and characterized through tensile testing, dynamic mechanical analysis (DMA), and differential scanning calorimetry (DSC). Subsequently, the films were interleaved with aramid fabric layers to manufacture the panels by autoclaving. Test specimens were obtained by waterjet cutting for flexural and impact resistance testing. The results showed that incorporating MMT20A clay significantly improved the composite properties. The sample with 1.0% MMT20A presented the highest tensile strength. In DMA, the samples with 1.0% and 5.0% MMT 20A exhibited higher loss modulus (E''), indicating greater energy dissipation capacity. DSC curves indicated an increase in the crystallinity of the nanostructured composites compared to pure HDPE. Finally, tests on laminated specimens revealed an increase in both impact and flexural strength with clay addition, reinforcing the potential of these materials for ballistic protection applications. The following steps in this study consist of Hopkinson bar testing and the production of multilayer panels by autoclaving for ballistic testing.

Keywords: High-density polyethylene. Aramid. Cloisite 20A montmorillonite clay. Nanocomposite. Laminates.

1. Introduction

The use of armor is of utmost importance in modern warfare, as well as in urban guerrilla contexts [1]. Ballistic barriers, especially when applied to personal protective equipment, require high mechanical properties combined with lightness and agility, ensuring user comfort and safety [1,2,3].

With the evolution of weaponry in recent years, laminated polymer composites have gained increasing prominence in ballistic applications [3]. The use of composite materials has led to significant advances in personal protection [4], considering that the addition of high-density polyethylene (HDPE) films has proven effective in laminated structures [2]. The use of nanofillers in polymer composites has shown effectiveness in improving mechanical properties without compromising processing or material density [3]. The incorporation of lamellar materials, such as montmorillonite, into polymer matrices is a viable option to ensure high mechanical and thermal performance of the polymer [2]. The use of MMT in thermoplastic matrix may be considered a promising ballistic solution due to the possibility of combining lightweight and ballistic resistance [5]. And even with a very low nanofiller content, it is possible to obtain high Young's modulus values for a thermoplastic matrix and a notable effect on the viscoelastic properties of the molten polymers [6].

Aramid fibers are widely applied in armor development [7]; thus, laminates with alternating layers of HDPE modified with Cloisite 20A montmorillonite clay and aramid were shaped in an autoclave, ensuring structural quality of the laminated composite during manufacturing by reducing void content [7].

Therefore, this work aims to evaluate the influence of adding different concentrations of Cloisite 20A montmorillonite clay on the mechanical and thermal properties of HDPE films and laminated composites through tensile testing, dynamic mechanical analysis (DMA), differential scanning calorimetry (DSC), and flexural and impact resistance tests. Dynamic mechanical analysis evaluates the response of a material to cyclic deformation as a function of temperature. It provides three main parameters: the storage modulus (E′), which represents the elastic response; the loss modulus (E″), which represents the plastic response; and tan δ (E″/E′), which indicates molecular mobility transitions such as the glass transition temperature [8].

2. Materials and Methods

2.1 Processing of composite films

Produced at the Materials Laboratory (LAMAT) of the University of Caxias do Sul (UCS), the materials were weighed, manually homogenized, and subsequently processed in a co-rotating twin-screw extruder, model MH-COR LAB, L/D 46, screw diameter of 20 mm, and length of 640 mm. The extruded material, after passing through a water tank, was pelleted in a knife mill. After a drying process, the material was extruded into films using a single-screw blown film extruder, model ES-35. HDPE (BF4810 from Braskem) polymer films with four different contents of MMT 20A clay were produced, in addition to the sample without filler addition, as shown in Table 1. The definition of the MMT 20A clay concentrations used in this study was based on previous works developed by the research group to which this study is linked. In particular, the work of Grison et al. [2] stands out, in which high-density polyethylene (HDPE) composites reinforced with different contents of Cloisite 30B montmorillonite (1%, 3%, and 5% by weight) were evaluated. Based on these findings, it was decided to investigate concentration ranges close to and slightly higher than those reported, using 1.0%, 2.5%, 5.0%, and 7.5% by weight of MMT 20A in order to evaluate the mechanical and thermal behavior of HDPE over a broader range of nanofiller contents, enabling the identification of an optimal concentration for ballistic applications.

The characterization of the films was carried out through tensile tests, dynamic mechanical analysis (DMA), and differential scanning calorimetry (DSC).

2.2 Production of laminated plates

Panels measuring 300 × 320 mm^2, composed of five layers of HDPE nanostructured with MMT 20A clay and six layers of aramid fabric (1129 TW 2040 840D, from Barrday), were produced using an autoclave process. Subsequently, specimens for flexural and impact resistance tests were obtained from the laminated panels by water jet cutting, as shown in Figure 1. The parameters applied in the autoclave processing are shown in Table 2.

2.3 Tensile testing of HDPE films modified with MMT clay 20A

Seven HDPE film specimens with different MMT 20A clay contents, measuring 165 × 25 mm^2, were subjected to tensile strength testing. The tests were performed at the Materials Laboratory (LAMAT) using an Emic DL2000 testing machine.

2.4 Dynamic mechanical analysis (DMA) in films of HDPE modified with MMT 20A clay

Dynamic mechanical analysis was used to determine the viscoelastic properties of the composites. Tests were conducted on samples with dimensions of 65 x 12.7 x 3.5 mm using the TA Instruments equipment, model DMA Q800, with a 3-point Bend clamp, at a temperature range of 23 to 130 °C, heating rate of 5 °C/min, and frequency of 1Hz. 65 x 12.7 x 3.5 mm^3.

2.5 Differential Scanning Calorimetry (DSC) in HDPE films modified with MMT 20A clay

Specimens of approximately 5 mg were subjected to differential scanning calorimetry (DSC) testing at the Materials Laboratory (LAMAT), using a DSC-60 (Shimadzu Corporation) equipment, with two heating runs (two cycles) in a temperature range from 23 °C to 250 °C, at heating and cooling rates of 10 °C·min^{-1}, and under a nitrogen flow rate of 50 mL·min^{-1}.

The degree of crystallinity of the material was calculated according to Equation 1, where X represents the degree of crystallinity, ARG% is the MMT 20A clay content in the sample, ΔHc is the measured melting enthalpy obtained from the melting peak area, and ΔHm is the melting enthalpy of 100% crystalline HDPE, equal to 293 J·g^{-1} [3].

$$Xc = \frac{1}{1 - ARG\%}\frac{\Delta Hc}{\Delta Hm}100\% \qquad (1)$$

2.6 Flexural strength test on laminated specimens

Flexural strength tests were performed at the Materials Laboratory (LAMAT) on a universal testing machine EMIC DL-2000, following ASTM D790 standard, using a 200 kgf load cell. The test was carried out on five specimens for each MMT 20A concentration, with dimensions of 127 × 12.7 × 1.5 mm³.

2.7 Impact strength test on laminated specimens

Charpy impact strength tests were conducted at the Mechanical Testing Laboratory (LAMEC) on five specimens for each MMT 20A concentration, with specimen dimensions of 63.5 × 12.7 × 1.5 mm^3. The impact test was conducted following adaptations of the ASTM D256-10 and ASTM E23-12C standards, carried out at LAMEC using a Veb Werkstoffprüfmaschinen Leipzig (Germany) testing machine. The test was performed with five specimens per sample.

3. Results and Discussion

3.1 Tensile test results for HDPE films modified with MMT 20A clay

From the analysis of Figure 2, it can be observed that tensile strength decreases with increasing montmorillonite clay content, with the highest average value recorded for the specimen containing 1% MMT 20A clay. However, samples with 5%, 2.5%, and 1% clay achieved average maximum stress values higher than those of the specimens without clay addition (HDPE). The increased particle agglomeration led to a more brittle material due to the formation of stress concentration points.

Figure 3 shows that specimens with 7.5% and 5% clay reached higher average modulus of elasticity values compared to those with 2.5% and 1% clay. Nevertheless, specimens with filler addition exhibited higher modulus values compared to the sample without filler.

3.2 Dynamic mechanical analysis (DMA) results for HDPE films modified with MMT 20A clay

Figure 4 presents the loss modulus of the HDPE samples modified with clay. The loss modulus (E'') represents the material's energy dissipation due to friction resulting from particle–particle and particle–polymer interactions. The graph shows that the addition of ARG to HDPE improves energy dissipation (loss modulus) up to a certain point, with 50% ARG standing out as the most efficient formulation. However, very high concentrations (75%) lead to a sharp decrease due to poor dispersion and possible embrittlement of the matrix.

3.3 Differential scanning calorimetry (DSC) results for HDPE films modified with MMT 20A clay

In Figure 5, the pure HDPE sample exhibits a melting temperature (Tm) of approximately 132 °C. However, modification with MMT 20A clay does not significantly change the Tm. On the other hand, the area under the DSC curve for the nanocomposites varied more, indicating changes in material crystallinity. Samples ARG10, ARG25, and ARG75 showed a 40% increase in crystallinity compared to HDPE without clay. The crystallinity values, calculated according to Equation 1, are presented in Table 3, along with Tm.

3.4 Flexural strength test results for laminated specimens

The flexural strength of the composites varied significantly depending on the MMT 20A content incorporated into the HDPE. The sample containing 7.5% clay (ARG75) achieved the highest average value, significantly outperforming pure HDPE and the other compositions. Moreover, samples ARG10 and ARG75 exhibited average flexural strength values higher than the sample without nanofillers, with increases of 20% and 172%, respectively. The flexural strength results are presented in Figure 6.

3.5 Impact strength test results for laminated specimens

The average impact strength values for pure HDPE and HDPE modified with MMT 20A are shown in Figure 7.

It is observed that the incorporation of nanofillers increased the impact strength for concentrations of 1.0% and 7.5% MMT 20A clay, with the highest value recorded for sample ARG10, which showed an 80% increase in impact strength compared to pure HDPE.

4. Conclusions

High-density polyethylene (HDPE) with different concentrations of MMT 20A montmorillonite clay was extruded and characterized through tensile strength tests, dynamic mechanical analysis (DMA), and differential scanning calorimetry (DSC). The tensile test indicated that samples containing 1% MMT 20A clay showed higher tensile strength than the other samples. However, with increasing clay content, a decreasing trend in tensile strength was observed. Even so, samples with 1%, 2.5%, and 5% MMT 20A clay exhibited higher tensile strength values than HDPE without clay addition.

DMA analysis indicated that the addition of MMT 20A clay up to 5 wt. % increased the material's energy dissipation capacity. These results suggest that clay addition enhances HDPE's impact properties, which is important for improving the ballistic performance of laminated composites produced with this film.

In the DSC test, an increase of up to 40% in crystallinity was observed for samples ARG10, ARG25, and ARG75 compared to pure HDPE.

Panels composed of alternating layers of aramid fabric and HDPE modified with MMT 20A clay were obtained via autoclaving. Specimens were cut from the panels using a waterjet and tested for flexural and impact resistance. Increases in both flexural and impact strength were observed for samples containing 1.0% and 7.5% MMT 20A clay.

The following steps involve Split Hopkinson Pressure Bar tests on multilayer specimens and the manufacturing of aramid/HDPE panels modified with MMT 20A clay for ballistic testing.

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Figures and tables

Table 1. Composition of the materials

Samples and Acronym	HDPE (wt.%)	Cloisite 20A (wt.%)
HDPE	100	0
ARG10	99	1
ARG25	97.5	2.5
ARG50	95	5
ARG75	92.5	7.5

Table 2. Autoclaving process parameters

Heating rate ramp (°C/min)	6
Maximum temperature (°C)	170
Time at maximum temperature (min)	85
Maximum pressure (bar)	7
Time at maximum pressure (min)	25
Cooling rate ramp (°C/min)	0.5
Final autoclave temperature (°C)	100

Table 3. DSC results for melting temperature and crystallinity

Samples	**Tm (°C)**	**Crystallinity (%)**
HDPE	132.0	37.0
ARG10	130.9	51.7
ARG25	131.4	51.8
ARG50	131.1	48.1
ARG75	131.4	51.7

Figure 1. Specimens obtained by waterjet cutting from multilayer panels.

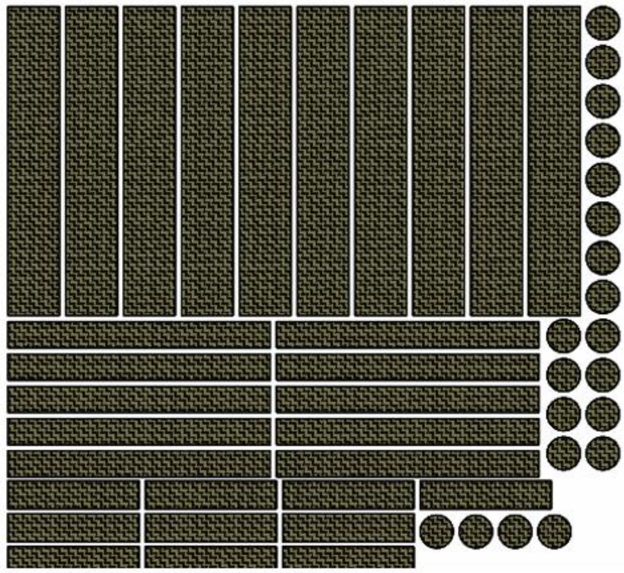


Figure 2. Tensile strength of HDPE modified with different MMT 20A clay contents.

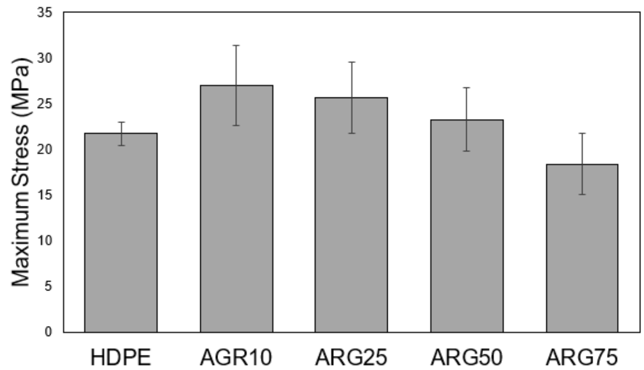


Figure 3 - Elastic modulus of HDPE modified with MMT 20A clay.

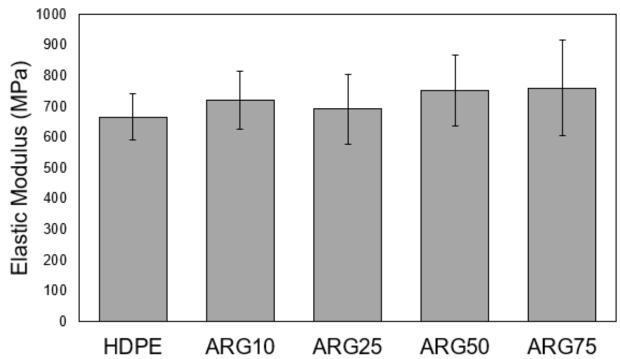
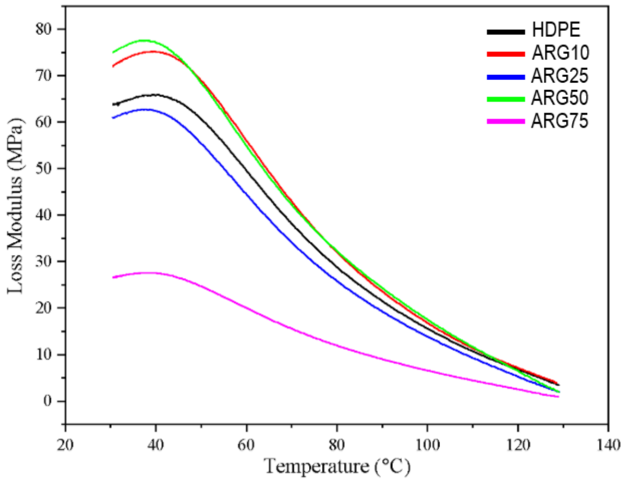


Figure 4. Loss modulus of HDPE specimens modified with MMT 20A clay.



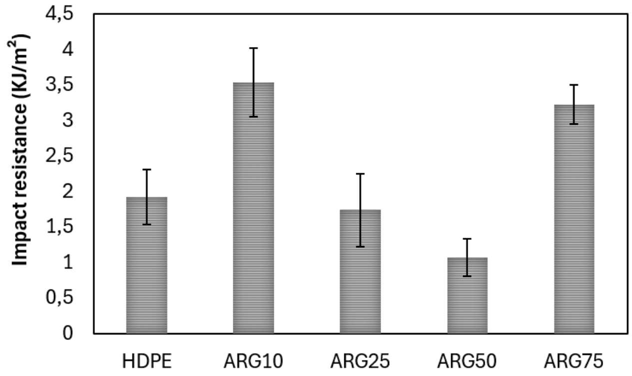


Figure 5. DSC curves for pure HDPE and HDPE modified with different MMT 20A clay contents.

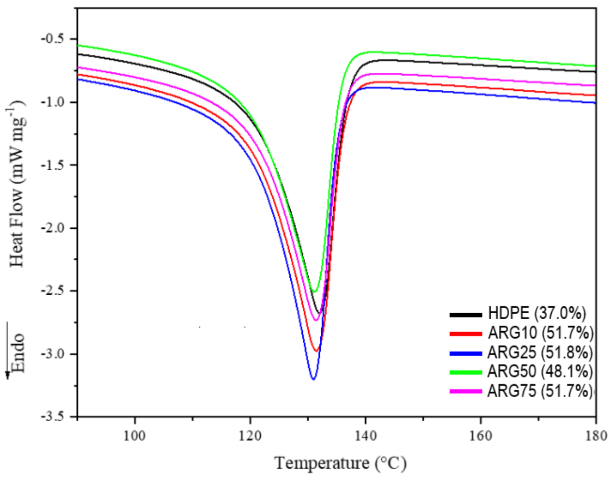


Figura 6. Flexural strength.

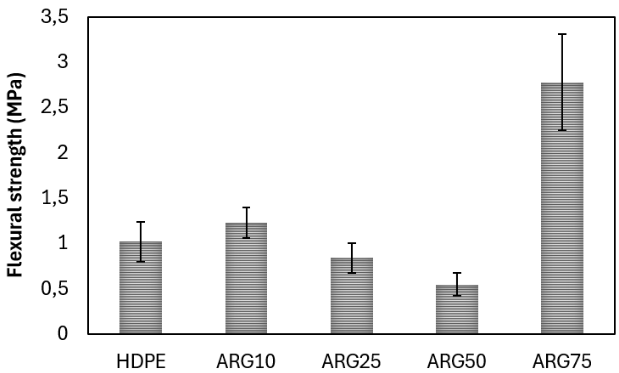


Figure 7. Impact strength.