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MECHANICAL CHARACTERIZATION OF POLYPROPYLENE COMPOSITES REINFORCED WITH ARGAN NUT SHELL PARTICLES

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Abstract

This study investigates the mechanical properties of a polypropylene (PP) composite reinforced with argan nut shell (ANS) bio-filler. Plates with different volume fractions and particle sizes were investigated through static bending tests and dynamic analyses (by DMA). The main objective of this study is to determine the best combination (volume fraction/particle size) to obtain the best material performance. The results showed that ANS particles improve the stiffness of PP by increasing The stiffness and storage modulus. The loss modulus also increased gradually, which means that the damping properties of PP were improved.

Keywords: Bio composite, Argan Nut Shell, Polypropylene, Mechanical properties, Four-point bending static test, Dynamic Mechanical Analysis, Damping properties.

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1 INTRODUCTION

Polypropylene PP is a thermoplastic polymer that is widely used in various industrial applications, such as packaging, automotive, and consumer goods due to its low cost, lightweight, and good chemical resistance [1]. However, its stiffness and strength are limiting factors for its use in structural applications requiring high properties. To overcome these limitations, PP composites reinforced with bio-fillers have been studied as an alternative material. The use of bio-fillers in composites is an environmentally friendly solution that can also improve the mechanical properties of the composite [2-4].

One promising bio-filler that has been studied is Argan Nut Shell (ANS). Argan nut shells are the hard outer casings that surround the edible kernel or seed of the argan fruit. The argan tree (Argania spinosa) is a fruit that originated in Morocco, and its nuts have been used for oil and other purposes for centuries [5]. The ANS has traditionally been used as a source of fuel for cooking and heating, as well as for making charcoal. However, it's worth noting that the use of argan nut shells for fuel and other purposes can have negative environmental impacts. It's important to use this resource responsibly and sustainably. The ANS is composed of cellulose, lignin, and hemicellulose, and it has been reported to have good mechanical properties such as high specific strength, and modulus [2,6]. Additionally, ANS is biodegradable and renewable, making it an attractive option for use in composites.

In this work, the static and dynamic mechanical properties of a PP reinforced with different volume fractions and particle sizes of ANS bio-filler were studied, to highlight their effect on the mechanical properties of neat PP, especially on the stiffness and damping properties of the PP/ANS composites.

This paper is organized as follows: Section 2 provides a description of the materials used in the study as well as a visualization of their microstructures. Section 3 outlines the methods that were employed to achieve the research objective. The results of the study are presented and analyzed in section 4. Finally, section 5 summarizes the conclusions that can be drawn from the research.

2 DESCRIPTION AND ANALYSIS OF MICROSTRUCTURES

2.1 Materials

The bio composite investigated in this study is composed of a PP polymer matrix reinforced with natural aggregates made from Argan nut shells (ANS) that are native to the south-west of Morocco. These shells are collected as residue after the extraction of the nut for the production of Argan oil. To obtain the aggregates, the shells were ground into powders with varying particle sizes (S1<0.15mm, S2<0.5mm and S3<1mm).

2.1.1 Chemical composition of ANS particles

The results obtained as given in Table 1 show that the shells of argan nuts are composed of three major components: cellulose, hemicelluloses and lignin. The rest of the composition includes extractables, water-soluble and ash (mineral matter).

ANS particles	Cellulose (%)	Hemicelluloses (%)	Lignin (%)	Ash (%)
	48	16	30	0.36

Table 1: Chemical composition of ANS particles

2.1.2 Thermal characterization of ANS particles

The thermal stability of ANS particles was studied by Thermal Gravimetric Analysis (TGA) and Derivative Thermogravimetry (DTG) under air from the ambient temperature to 600 °C. The plots figured in Fig 1 show weight loss in three stages. The first stage, which results in a weight loss of approximately 5%, occurs at 96°C, and is attributed to the evaporation of water from the particles. The onset of degradation for the ANS particles, on the other hand, occurs after 235°C. Above this temperature, the thermal stability of the particles gradually decreases, leading to their degradation. The first peak of degradation at 273°C is associated with the degradation of hemicelluloses [7]. The second strong peak occurs at 341°C and corresponds to the degradation of cellulose [8].

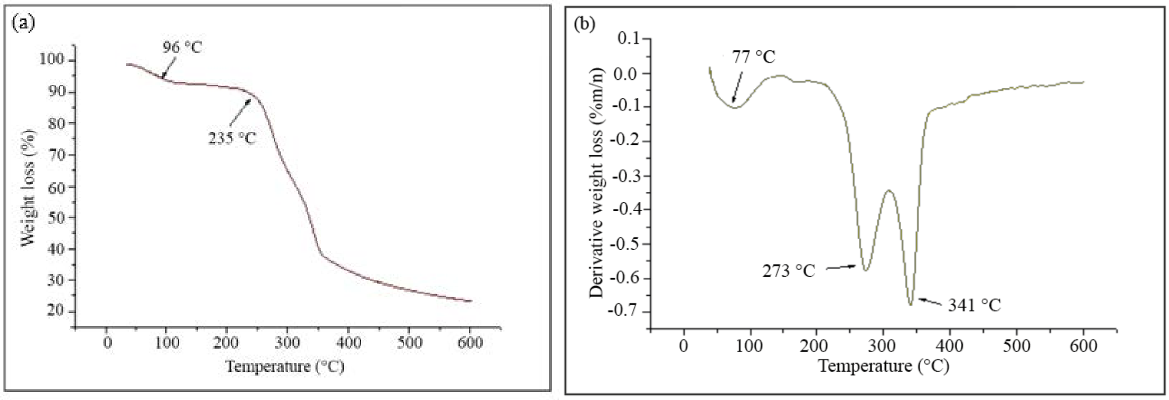

Fig 1: (a) TGA curve (b) DTG curve of ANS particles

2.2 Composites preparation

The composite was made by blending PP with 5wt%, 10wt%, and 15wt% ANS particles using an extrusion process. Then the samples were made using injection molding to form plates of 100x100x2mm as shown in Fig 2.

The thermoplastic PP used in the composite has a density of 0.9 g.cm^{-3}, a melting temperature range of 150-170°C, a Poisson ratio of 0.4, and Young's modulus of 1 700MPa. In contrast, the ANS particles have a density of 1.29 g.cm^{-3}, and Young's modulus of 8 000MPa [9].

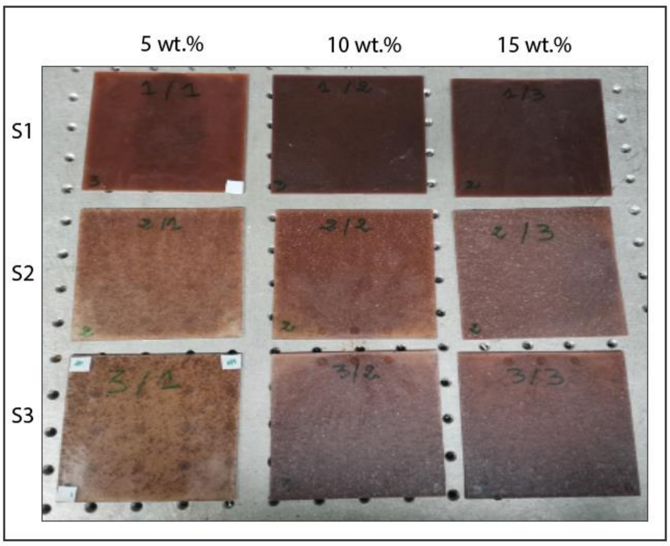

Fig 2: Plates of PP/ANS with 5wt%, 10wt% and 15wt% volume fraction and three particle sizes S1, S2 and S3

2.3 Microstructural analysis

Scanning Electron Microscopy SEM was used to evaluate the particle dispersion/distribution in the PP matrix and to illustrate the morphology of ANS particles, using JEOL IT 100 SEM. All composite samples were cut into small pieces and metalized with a thin layer of gold to make them conductive and allow to the beam of electrons to interact with atoms of the samples.

The SEM analysis of ANS particle distribution within the PP matrix shown in Fig 3 (a) and (b) revealed that there was no significant clustering or aggregation of ANS particles. This is an important observation because particle clustering can result in non-uniform dispersion within the matrix, which can negatively impact the mechanical and thermal properties of the composite material. The lack of agglomeration observed in this study suggests that the ANS particles were effectively dispersed and mixed with the PP matrix during the fabrication process. This can be attributed to the relatively uniform size and shape of the ANS particles given in Fig 3 (b) and (c), which allowed for easier dispersion into the matrix. Additionally, the strong surface adhesion between the ANS particles and the PP matrix promotes their effective dispersion, preventing the formation of clusters and improving the uniform distribution of particles within the matrix. This uniform distribution of ANS particles with strong surface adhesion can lead to a more consistent composite material with improved mechanical properties. [10,11]

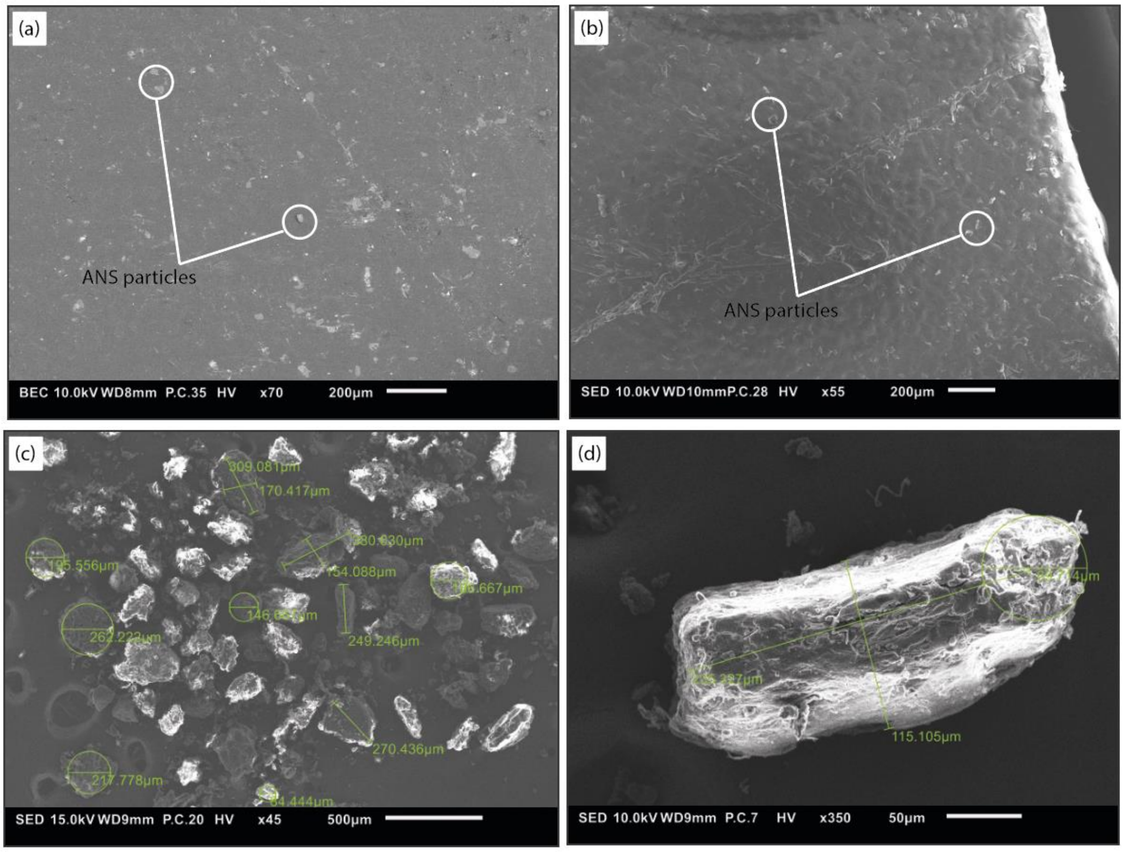

Fig 3: SEM images of PP composites containing (a) 5wt%-S1 ANS particles (b) 10wt%-S2 ANS particles (c) ANS particles (d) solo ANS particle

3 CHARACTERIZATION TECHNIQUES

3.1 Bending static tests

As shown in Fig 4-(a), four-point bending tests were carried out to reach the material stiffness. The bio-composite plates were fixed from 3 corners and the fourth one was loaded with a 60g load. The loading-unloading process was done with 20g steps loading speed. The tests were performed in a room with an average temperature of 23.4±1.2 °C, and an average humidity of 52.85±2.05 %RH. The loaded corner displacement was measured using Laser Displacement Meter LC-2400A as shown in Fig 4-(b). Fig 4-(c) displays the loading-unloading process of the plates up to a load of 60g.

The bending tests were performed on a total of thirty plates, consisting of nine batches of PP/ANS composite plates with varying volume fractions and particle sizes as outlined in Table 2, in addition to neat PP plates. Each batch comprised three plates, so that the average displacement with standard deviation could be reported.

	5wt%	10wt%	15wt%
S1	1/1	1/2	1/3
S2	2/1	2/2	2/3
S3	3/1	3/2	3/3

Table 2: Number of samples tested on the bending test

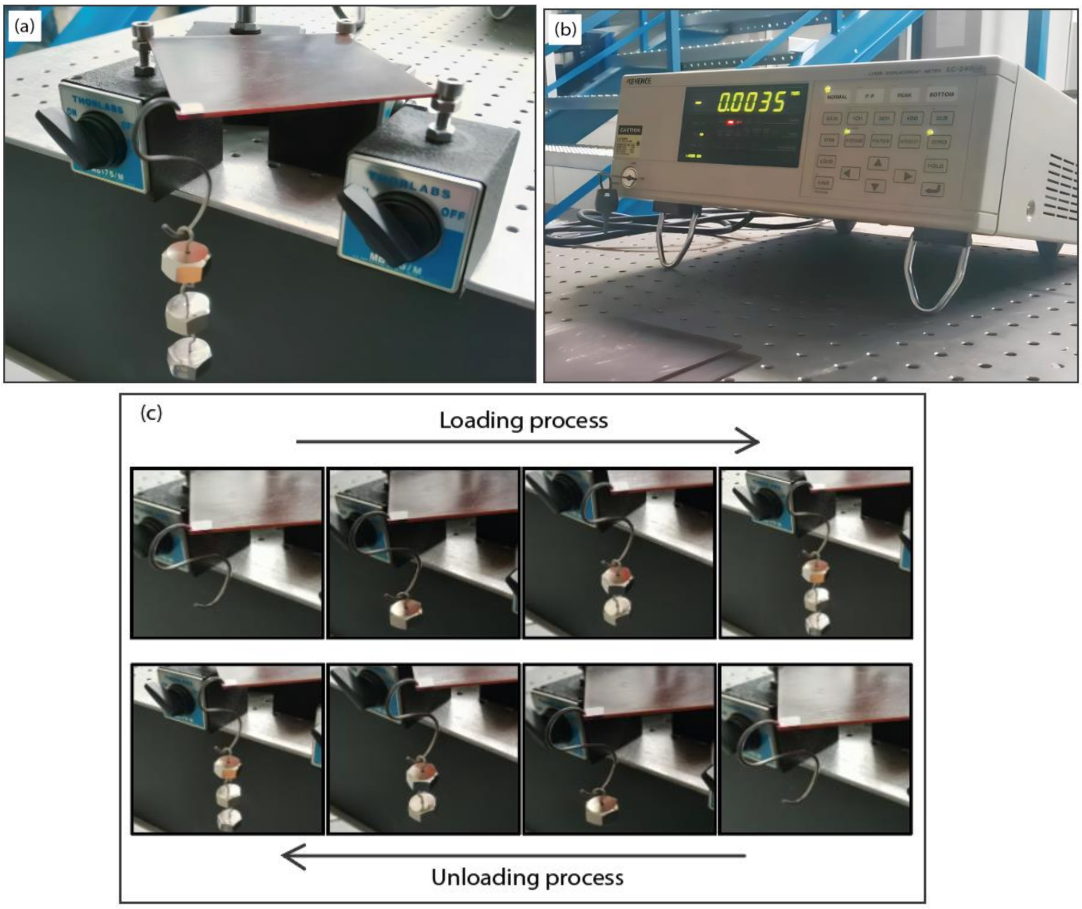

Fig 4: Configuration of static test of PP/ANS composite plates (a) Four-point bending test (b) Displacement measurement by Laser Displacement Meter LC-2400A (c) Loading and unloading process of the plates with 20g steps up to a load of 60g

3.2 Dynamic Mechanical Analysis

Dynamic Mechanical Analysis (DMA) tests were performed using TA Instruments Model Q800 dynamic mechanical analyzer. The experiments were carried out using a single cantilever configuration on samples of 17.5x14.9x2mm at a fixed temperature of 25°C. The multi-frequency strain test was performed using a strain amplitude of 0.0015 in a frequency range of 0.1 to 100 Hz.

4 RESULTS AND DISCUSSION

4.1 Static properties

The resulting curve in Fig 5 shows a hysteresis shape, indicating energy loss during the deflection and the presence of a viscoelastic behavior [12]. The results showed that the PP/ANS composites withstood deflection more than neat PP which means that the addition of ANS particles improved the stiffness of the material. The composites with ANS particles exhibited a higher slope of the force-displacement curve than the pure PP matrix, indicating increased rigidity of the material. This behavior can be attributed to the interaction between the ANS particles and the PP matrix, which can lead to frictional losses and energy dissipation during the deformation process [13].

It can be concluded from Fig 6 that PP 1/3 has the highest stiffness and the PP1/1 and PP 1/2 are stiffer than the other plates of particle sizes S2 and S3. The reason for this difference in stiffness is explained by the surface area of adhesion between the PP particles and the matrix [14]. When the particle size is smaller, there is more surface area available for adhesion with the matrix. This results in a more homogeneous structure, as the particles are evenly distributed throughout the material and provide more points of contact with the matrix. This increased contact area results in higher stiffness and better resistance to deformation under stress. On the other hand, larger particle sizes have a higher probability of clustering together within the matrix as shown in Fig 7. This can lead to a less uniform structure, as the particles are not evenly distributed throughout the material. As a result, there is less surface area available for adhesion with the matrix, resulting in lower stiffness and reduced resistance to deformation under stress [15].

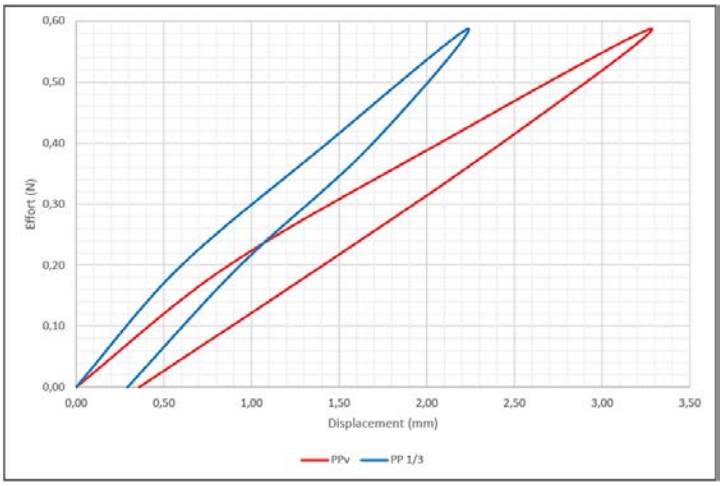

Fig 5: Behavior of PP/ANS 1/3 composites compared to neat PP behavior

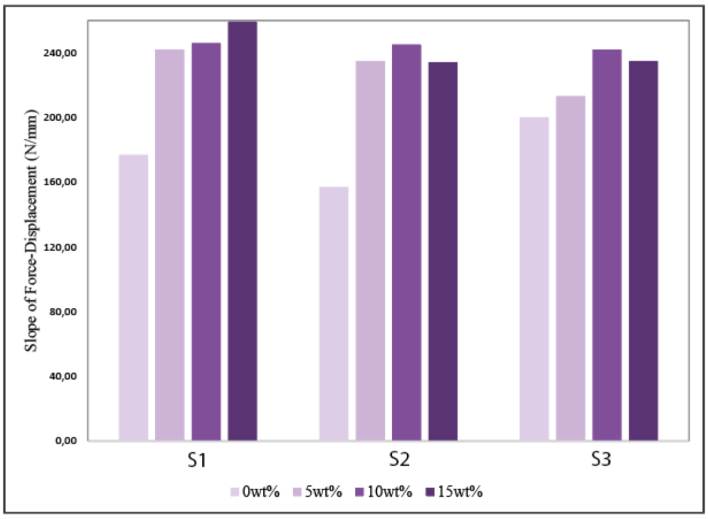

Fig 6: Variation of the slope of Force-Displacement curve of PP/ANS composites compared to neat PP (0wt%).

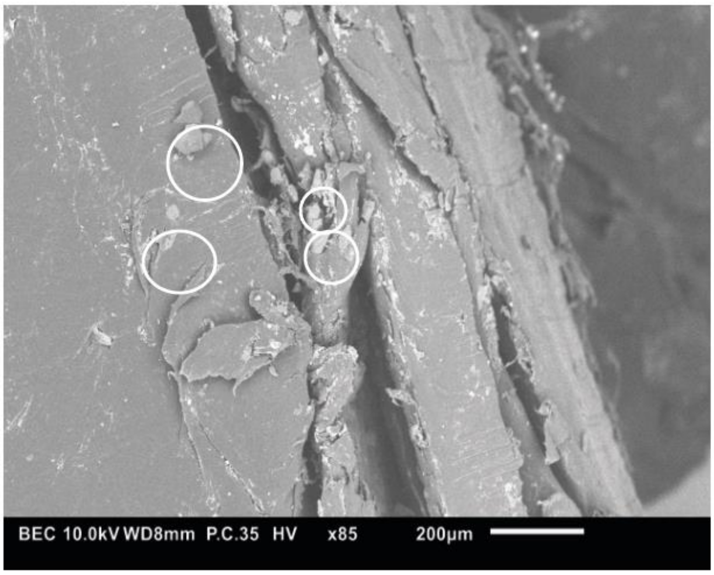

Fig 7: SEM images of ANS Aggregates clustering in PP 3/3

4.2 Dynamic mechanical properties

The DMA gives a clear idea about the viscoelastic properties as well as the phase structure of blends. A comparison of the dynamic properties of neat PP and PP/ANS composites is given in this section. The plot of storage modulus denoted E' versus frequency represents the frequency response of elasticity. Whereas, the plot of the loss modulus denoted E" against frequency indicates the viscous behavior.

The results presented in Fig 8, 9, and 10 show that an increase in the volume fraction of ANS particles (from 0wt% to 15wt%) leads to an increase in E' and E" for all particle sizes tested (S1, S2, and S3). The incorporation of ANS particles increased the dynamic moduli compared to the neat PP. This increase in storage modulus indicates the elastic behavior of the composites. Moreover, when the stress is applied to a composite material, the reinforcement transfers the load to the matrix. If the stress transfer is efficient, the matrix is able to resist deformation and store energy, which increases the storage modulus [16]. However, it should be noted that the storage modulus decreased for large particles (S2 and S3) with high-volume fractions. That can be caused by the aggregation of particles and low surface adhesion between the matrix and the filler as shown in Fig 7.

The storage modulus increased after excitation, and this is arising from the fact that at high frequency, the external force is applied more rapidly than the polymer chains can respond, so the polymer chains don't have enough time to rearrange and the energy is stored as elastic energy [17]. The loss modulus increased as well linearly with frequency, this is due to the increase in relative motion between polymer chains that leads to more internal friction between polymer chains and energy dissipation as heat, resulting in a higher loss modulus [18].

The loss factor is defined as the ratio of the loss modulus to the storage modulus and is a measure of the material's damping behavior. It is observed that the tan delta barely decreased with the incorporation of ANS filler. That could be explained as that the increase in the storage modulus was a bit larger than the increase in the loss modulus. This decrease indicates that the elastic behavior prevails over the viscous one given that, the storage modulus measures the elastic part of the material and the loss modulus represents the viscous part of the viscoelastic material [19–21].

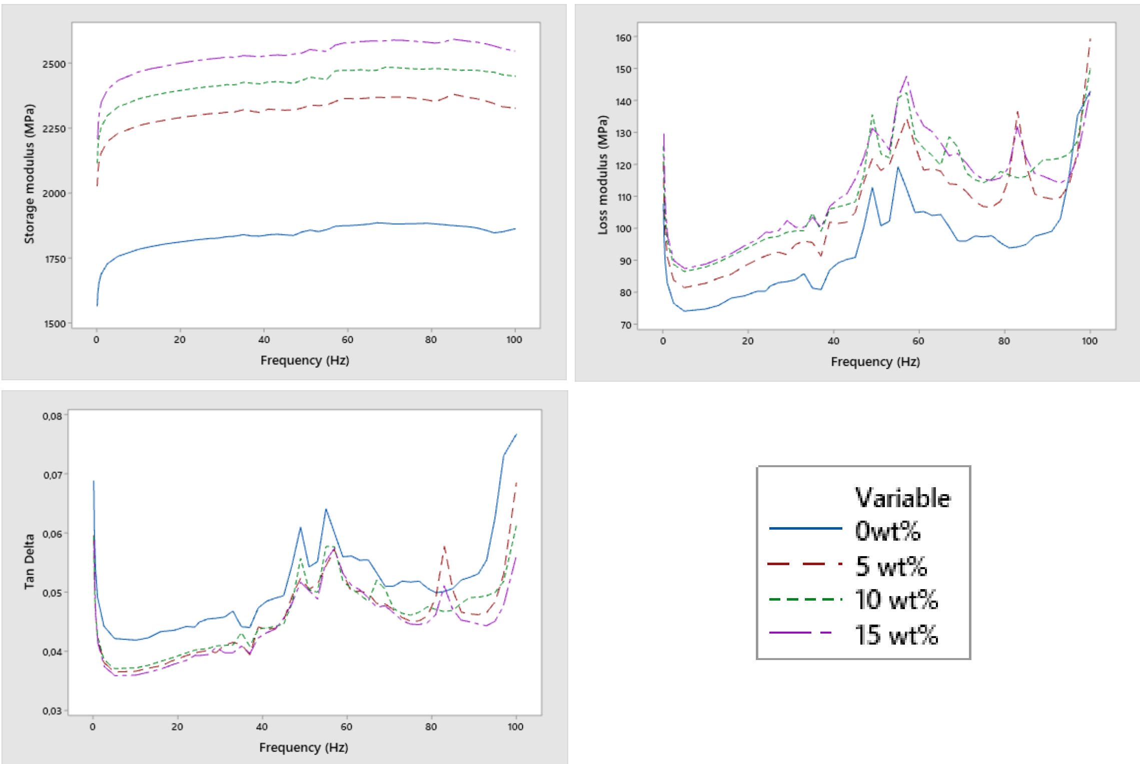

Fig 8: Dynamic properties of PP/ANS composites for particle size S1: Storage and Loss moduli and Loss factor

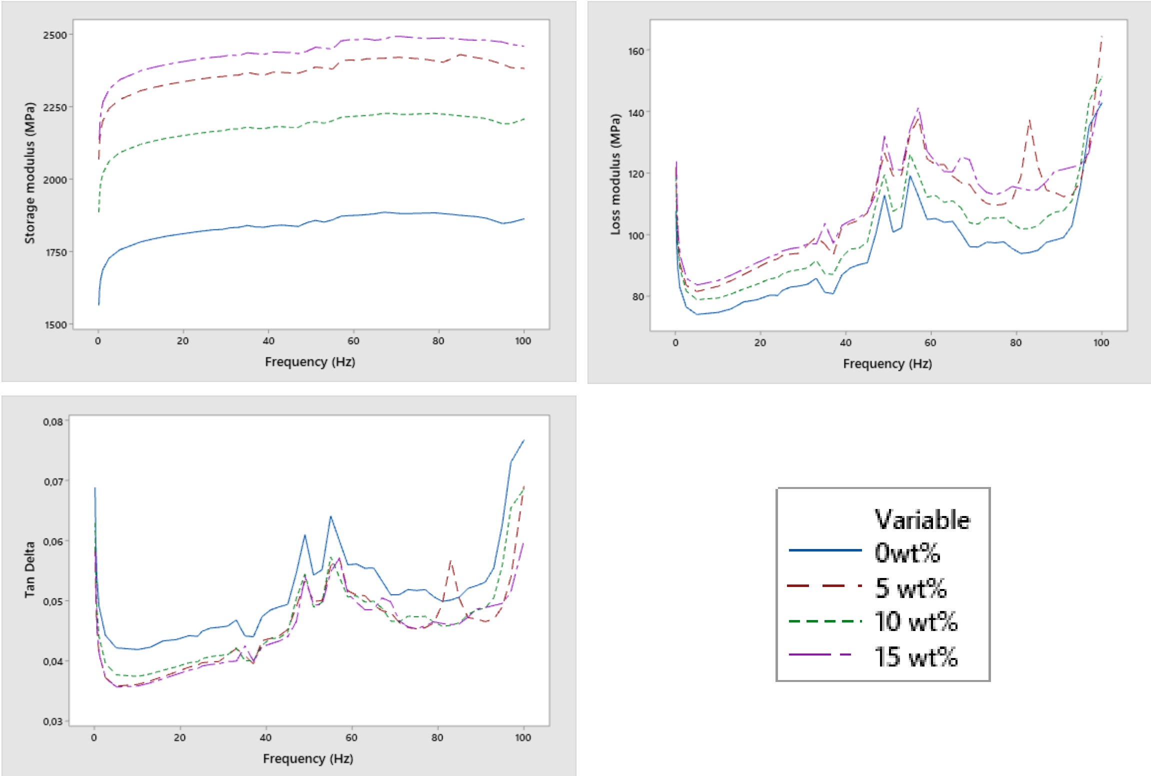

Fig 9: Dynamic properties of PP/ANS composites for particle size S2: Storage and Loss moduli and Loss factor

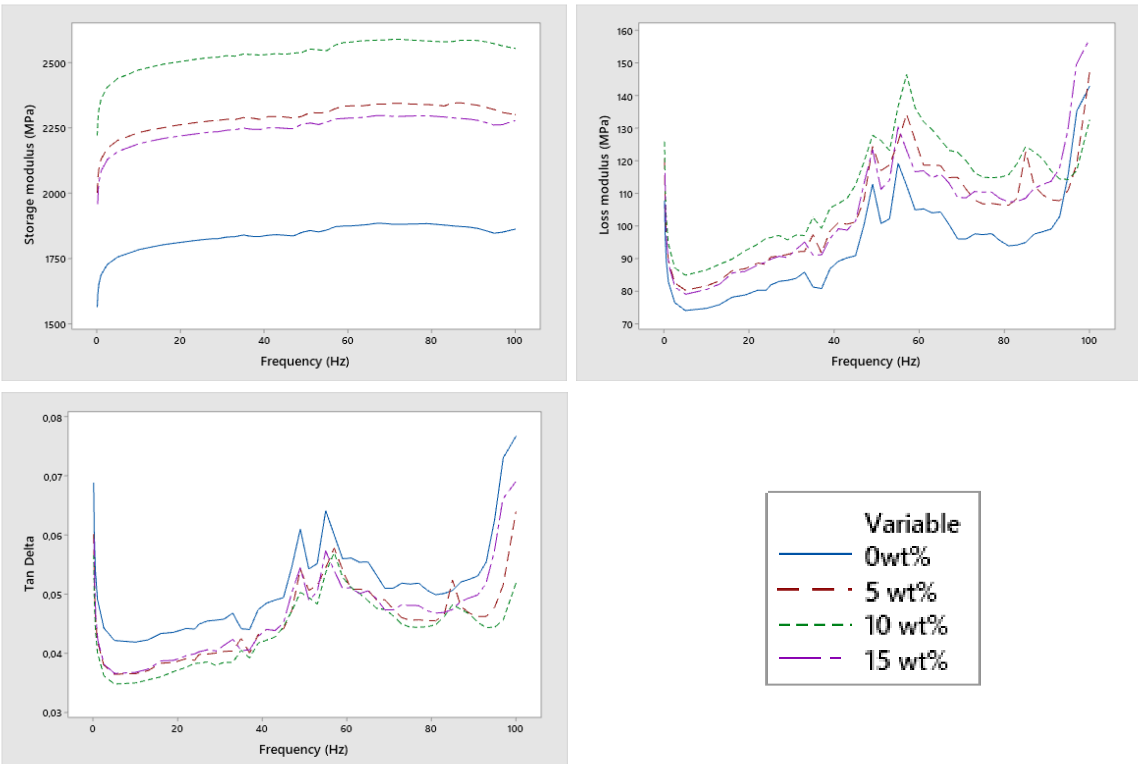

Fig 10: Dynamic properties of PP/ANS composites for particle size S3: Storage and Loss moduli and Loss factor

5 CONCLUSIONS

Numerous projects are being funded to explore advanced applications of Moroccan natural resource ANS as a filler in polymer matrices, due to their potential to create ecological products with high performance and low cost. The present study focuses on investigating the structural, and mechanical properties of ANS, a bio-filler that reinforces the PP matrix.

The addition of ANS particles to the PP matrix of the composite improved the stiffness and resistance to deformation under stress. The smaller particle sizes with high volume fractions (15wt%-S1 in this study) resulted in a more homogeneous structure with increased surface area for adhesion to the matrix, leading to higher stiffness. Additionally, the PP/ANS composites provide an increase in the storage modulus and loss modulus compared to neat PP. Moreover, it was observed that the rigidity and the damping properties of the material increased at high frequencies, whereas the tan delta of the composites remained unchanged during excitation. These observations suggest that the inclusion of ANS particles in PP composites can lead to improved mechanical properties and potential for use in structural applications.

6 ACKNOWLEDGMENTS

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