

# Thermal, mechanical and rheological properties of HDPE/ Nut-shells of argan composite

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## ABSTRACT

**Mechanical, thermal and rheological properties of high-density polyethylene (HDPE)/ Nut-shells of Argan (NA) particles composites were investigated to see the effect of adding coupling agent and particles content on the composites properties. HDPE/NA particles composites formulations were melt-blended using a twin-screw mixer. The thermal behavior of NA particles reinforced HDPE composites was studied by thermogravimetric. The effects of particles content on the thermal properties were evaluated. It was found that at high temperature NA particles degrades before the HDPE polymer. The experimental results of mechanical properties from this investigation indicate that the ductility and toughness decrease with increasing NA particles content, but raising substantially its rigidity. In the event the tensile properties were significantly improved with the addition of compatibilizing agent, being in accordance with the mechanical results. The results of rheological properties show that there is no significant increase of storage and loss modulus with the addition of 3 wt.% of agent coupling maleic anhydride grafted polyethylene (PE-g-MA) on the composite (with 15wt.% of NA particles). But, there is an increase of the frequency of the crossover compared to the virgin matrix.**

**Keywords:** Thermal properties, Mechanical properties, Rheological properties, High density polyethylene, Nut-shells of Argan, composites.

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## 1. INTRODUCTION

The high usage of mineral, non-recyclable and unsustainable materials in industry leads to its depletion, increasing their prices and producing polluting waste difficult to get rid of. This made us think of other materials derived from sustainable sources to produce ecological materials [1]. Recently, there has been an increasing interest in the development and use of thermoplastic materials based mainly on the polymer matrix reinforced with natural substances. The effects of natural fillers on thermal, mechanical and rheological properties of matrix polymer composites related to several of factors such as load concentration, load shape and particle size, adhesion between filler and polymer and filler dispersion in the polymer matrix [2,3,17]. However, the compatibility of the composite depends on the hydrophilic character of natural fillers and hydrophobic character of polymer matrix [4]. Polymer modification and chemical treatment of the filler improve and provide good interfacial adhesion and also enhance the properties of the composite [5]. Several researches has been done on the reinforcement by natural load, such as coir [6], banana [7], wood fiber [21], alfa [8], flax [9], rice hull [17]. The composite of plastic and wood is the appropriate filler due to its renewability, abundant availability and its biodegradability. Nut-shell of argan is one of the major residues after argan oil production which annually accumulates in large volumes in kingdom of Morocco. The Nut-shell of argan is used basically in combustion.

The purpose of this study is to value the Nut-shell of argan by using it as a filler in the composite and determine the effect of the rate of reinforcements of Nut-shell of argan particles and the addition of coupling agent of PE-g-MA on the thermal, mechanical and rheological properties of HDPE/ Nut-shells of argan composite.

## 2. MATERIALS AND METHODS

### A. Materials

The particles of Nut-shells of Argan (NA) used in this work are from rural areas of south-west of Morocco. The polymer matrix is a high-density polyethylene (HDPE) (SclairA59) whose melting temperature is 135°C and a density of 980 Kg /m<sup>3</sup>. The coupling agent is Fusabond 226DE Dupont. It is a maleic anhydride grafted polyethylene which melts at 120°C and has a melt flow index of 1.5 g/10 min (190 °C, 2.16 Kg).The amount of the coupling agent used is 3% of the total

weight of the composite. It is the optimal amount to improve the homogeneity of the mixture ensuring better distribution of the particles in the polymer matrix. The previously dried Nut-shells of Argan were ground into particles. These particles were dried at 105°C for 24h to get a moisture level of 2–3% then stored in polyethylene bags. The residual moisture content is calculated from the mass of particles before and after a second drying at 120 °C for 24 hours.

#### **B. Preparation of the composites**

In this study a series of HDPE/NA particles blends with the percentage by weight of 0%, 15%, 30%, 45% were prepared using an internal mixer (Haake Rheomix 600 with roller-type rotors) with screws speed of 100 rpm at temperature of 170 °C. This temperature is selected to remain below a degradation temperature of the particles. Firstly, the matrix polymer HDPE and the compatibilizer PE-g-MA were introduced and mixed together for 2 minutes which ensured a complete melting of the polymer blend. Secondly, the particles were introduced and kneaded for 5 minutes. Four different content by weight of particles were investigated: 0%, 15%, 30%, 45%. Pellets and test specimens were taken for the rheology and the tensile tests respectively. They were fabricated using a heating press set at a temperature of 150°C, and a mold constituted of aluminum plates. In order to ensure the melting of the matrix which is preload, we applied a pressure for two minutes, followed by a compression until 8 MPa during four minutes for manufacturing of the samples.

#### **C. Particle size measurement**

A particle size analyzer (Malvern mastersizer 2000) was used to determine the average particle size and the size distribution of the particles of Nut-shells of Argan. The principle of this technique is based on the diffraction and scattering of a laser beam to determine the particle size.

#### **D. Thermogravimetric analysis (TGA)**

The thermal decomposition of HDPE and particles of Nut-shells of argan composite was evaluated by thermogravimetric analysis (TGA). The thermal stability was determined using a TGA Q500 series thermogravimetric analyser (TA Instruments, USA). Samples of approximately 10 mg were placed into a platinum pan and heated from 0°C to 600°C at 10°C/min, under nitrogen atmosphere

#### **E. Tensile tests**

Rectangular specimens having dimensions of 125mm x15mm x5 mm were used for the tensile properties. The specimens were evaluated by mechanical tests to investigate the elasticity modulus (E), tensile strength (Rm) and elongation at break ( $\epsilon_r$ ) allowing the comparison between the mechanical performances with the various NA particles content in the HDPE samples. The tensile properties were measured according to ASTM D 5456 standard with a universal testing machine Zwick/Z2,5 with 2,5 kN capacity, at a crosshead speed of 3 mm/min and at room temperature. Each value obtained represented the average of three samples of each category.

#### **F. Rheological analysis**

The rheological properties were measured using a RheoStress RS75. The tests were performed with plate-plate geometry of (diameter: 20 mm, gap: 3mm). The pellets samples were molded according to the diameter of the plate. The experiment was performed at 170°C over the frequency range from 0.1Hz to 100Hz. The deformation of 4% and 1% in strain amplitude for the matrix polymer and the composite with 15% of filler respectively, were chosen the low strain rate so to ensure the linear viscoelasticity of the dynamic tests.

### **3. RESULTS AND DISCUSSION**

#### **G. Particle sizes of Nut-shells of Argan**

Figure 1 (a) illustrates the distribution curve of particle sizes in the Nut-shells flour acquired from the particle size analyzer. NA flour is obtained by grinding Nut-shells of argan. The average size of the Nut-shells particle was 61  $\mu\text{m}$ . (b) shows microscopically the particles of Nut-shells of argan used in the present study.

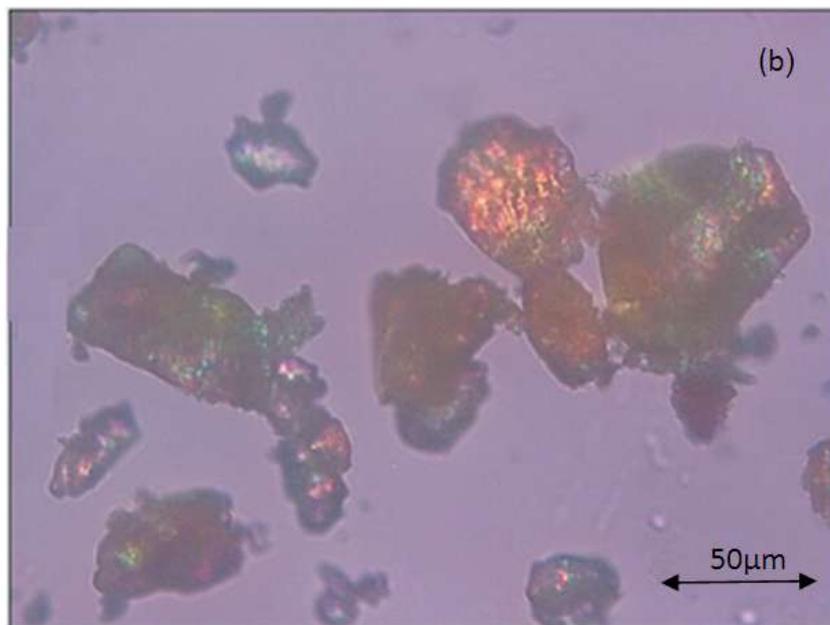
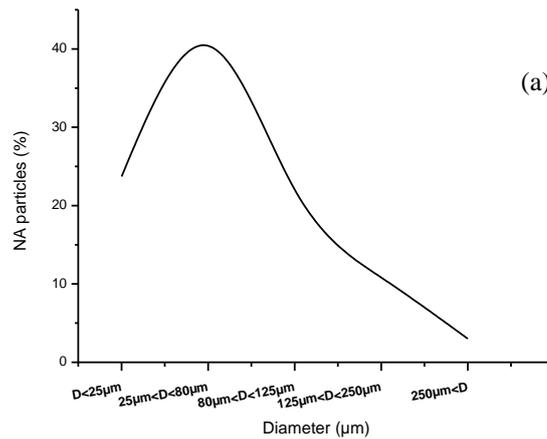


Figure 1.

Figure 1. Micrograph (b) and the particle size distribution (a) of the Nut-shells of Argan particles.

## H. Thermal analysis

Fig. 2 shows the thermogravimetric curves of pure HDPE, pure NA particles and the reinforced composite (at 15, 30 and 45wt.% particle content). The Nut-shells of Argan particles present three decomposition steps: the first decomposition is between 50°C and 100°C, which corresponds to the vaporization of water in the sample leading to a loss of 3% of its initial weight. The second decomposition of NA particles occurred at the temperature range of 220°C to 350°C, corresponding to the thermal depolymerisation of hemicelluloses, and degradation of pectin and the lignin (weight loss of 47.5%) [22,23]. The third decomposition at 350°C is associated to the thermal degradation of cellulose and lignin. The decomposition of this latter takes place in a wide temperature range 200°C to 600°C [24,25,26]. Above a temperature of 600°C, the residual char is found [27]. The decomposition of virgin HDPE showed a single stage in the range of 400°C to 490°C or it is completely disappeared due to the transformation of HDPE in to a gas at higher temperature. In HDPE/ NA particles composites, the decomposition occurs in two main processes, as shown above in TGA curve of the composite at 15, 30 and 45 wt. % particles contents. The first thermal degradation corresponded to the decomposition of major constituents in the NA particles in the range 240 to 350°C and the weight loss HDPE/NA particles composite decreased with greater NA particles content at the time when the second degradation related to the thermal decomposition of the neat HDPE in the range 400 to 490°C. It was also noted that increasing contents of NA particles in HDPE/NA particles composite gives more residue.

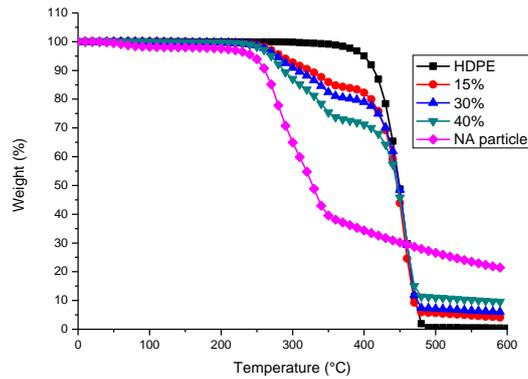
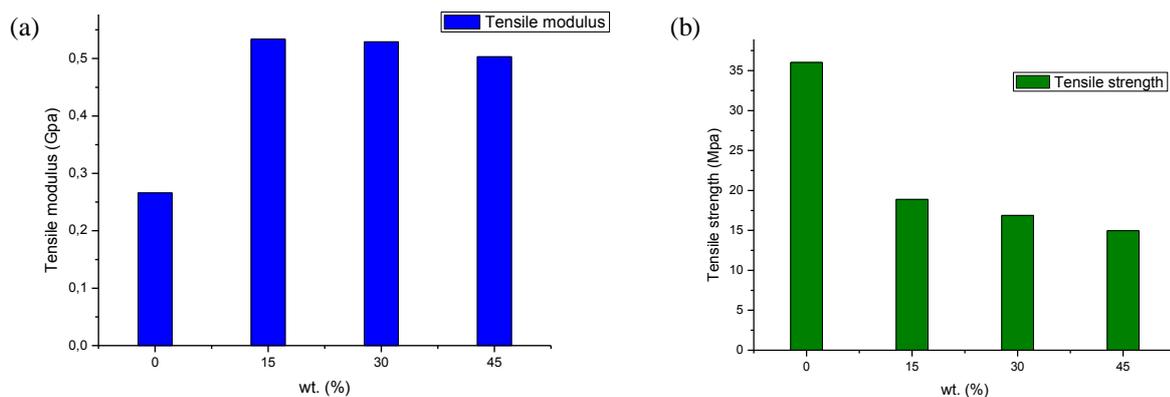


Figure 2. TGA thermograms of different percentage of Nut-shells of Argan particles in HDPE matrix composites, neat HDPE and NA particles.

### I. Tensile properties

Fig. 3 shows the variation of various mechanical properties as a function of NA particles content in the composites. The PE-g-MA content was set at 3 %. Fig. 3 (b) show that the tensile strength progressively decreased with the increase of NA particle content. This could be caused by poor interfacial adhesion between the HDPE matrix and NA particles. This suggests that there is low stress transferring from the matrix to the particles owing to incompatibility between the different components of the composite. In Fig. 3 (a) the histogram shows that the tensile modulus was also significantly influenced by NA particles concentration. Then, the young's modulus increases with the increase of the particle content. This improvement in modulus reached a maximum value of about 534Mp by increasing NA particles content up to 15% and then decreases steadily with the increase of particles content, which can be explained, first, by good adhesion between NA particles and polymer, and, second, the stiffness of particles which is higher than that of HDPE polymer. The small decrease in the tensile modulus is the consequence of the formation of the agglomerations of the NA particles in the highly loaded composites and larger particles of NA brings about large cavities at the contact surface between the matrix and the filler. This leads to a decrease in the wettability between polymer and particles, and an increase in the stiffness of the composite which explains the decrease in the modulus of elasticity. In Fig. 3 (c) the elongation at break mainly depends on the NA particles content. Elongation decreases steadily with the increase of the filler content from 9.4 to 3.5% when incorporating only 15% of NA particles due to poor adhesion between the polymer and particles, and brittle behavior of NA particles component in the composites. The histogram of Fig. 3 (d) shows the necessary work at break of composites. The toughness decreases with increasing the NA particles content, which makes the composite rigid but brittle. Generally, the alteration of the composites by particles decreases their ductility. The reinforcements also will cause stress concentration, and can reduce the mobility of polymer chain thus restricts its movement [15]. A rather similar behavior was also reported by [16, 17, 18, 19, 20, 21].



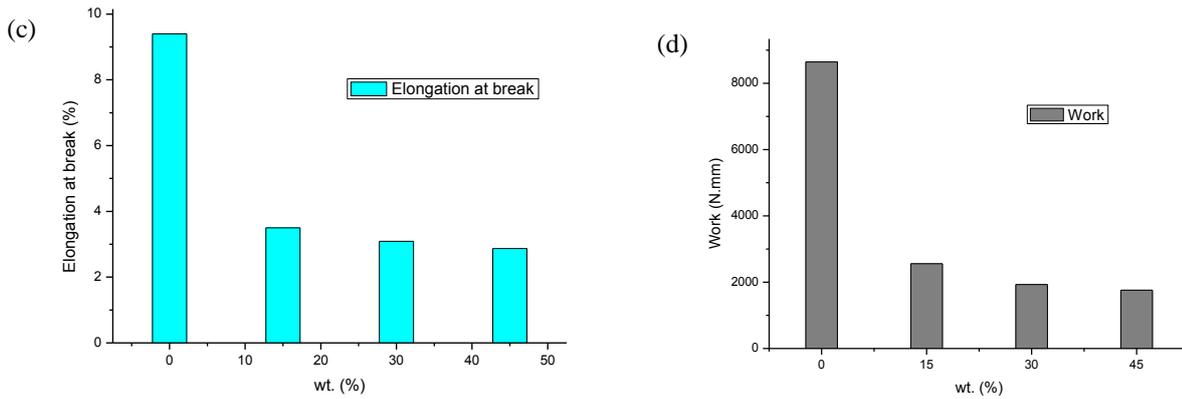


Figure 3. Mechanical properties of HDPE/NA particle composite.

Table 1: Tensile properties of HDPE/NA particle composite with and without PE-g-MA.

NA particle content (wt.%)	PE-g-MA (%)	E[Gpa]	Rm[Mpa]	$\epsilon_r$ [%]	W[N.mm]
0	0	0,266±0,009	36.04±2.11	9.4±2.36	8648±83
15	0	0.377±0.037	15.748±1.76	4.55±0.67	3074±700
15	3	0.534±0.058	18.87±0.95	3.5±0.52	2560±548

Table 1 shows the effect of PE-g-MA on the tensile properties of the HDPE and NA particles (85/15 by wt.) composites. The composite containing 15% NA particles was chosen to investigate the effect of compatibilizer on the tensile properties of the composite. The tensile strength and young's modulus has increased by 19.8% and 41.6% respectively, compared to composite without PE-g-MA. This improvement is owing to the compatibility between the polymer and NA particles and, to a good dispersion of hard particles in the continuous HDPE phase. The use of PE-g-MA enhances interaction and adhesion between the particles and polymer leading to better stress transferring from the polymer to the particles because the NA particle is more rigid than the polymer. This improvement of the wettability between particles and matrix polymer leads to a decrease in the stiffness of the composite resulting in a decrease of elongation at break and rupture energy.

#### J. Rheological analysis

The variation of dynamic storage modulus  $G'$  and loss modulus  $G''$  is a function of frequency is illustrated in fig. 4 (a). It is clear that both modulus  $G'$  and  $G''$  increased linearly with the increase in frequency. At a low frequency, the polymer chains have sufficient time to be fully relaxed and the presence of yield stress resulting from the formation of an interconnected particle network in the polymer matrix [14]. This high relaxation tends to reduce the  $G'$  and  $G''$  values. At a high frequency, the entangled chains have less time to re-oriented which is increases the modulus [13]. At a low frequency, the comparison between  $G'$  and  $G''$  shows that loss modulus is higher than storage modulus in all cases: pure matrix and composite with and without PE-g-MA, which gives the composite a viscous behavior. Beyond crossover frequency,  $G'$  becomes higher than  $G''$  for all pellets which gives the composite an elastic behavior. The addition of NA particles with and without PE-g-MA into matrix HDPE increases crossover frequency, this increase leads to a loss of elasticity of the composite due to the higher rigidity of NA particles than those of matrix HDPE [12]. This increase of the viscous behavior of the composite is also due to the friction between particles and matrix HDPE [12]. Fig. 4 (b) shows the complex viscosity  $\eta^*$  curves as a function of frequency of the composite HDPE/NA particles with and without PE-g-MA with a fixed filler content at 15 wt.%. The presence of filler in the matrix has no significant effect on the viscosity evolution curves, but the complex viscosity decreases with the increase of frequency. This phenomenon is primarily attributed to a shear thinning effect, and also due to the low loading of NA particles in polymer matrix, coupling agent, shape of filler and particle size. Therefore, the flow of the blend needs more shear stress and relaxation time [10, 11, 12, 14].

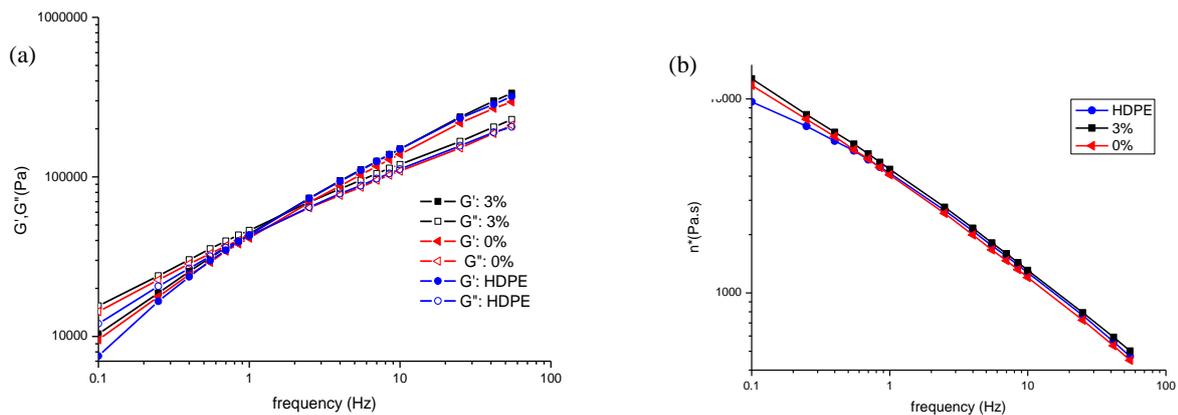


Figure 4. (a) Storage ( $G'$ ) and loss modulus ( $G''$ ) and (b) complex viscosity ( $n^*$ ) of the composite filler at 15% of NA particles with and without PE-g-MA.

#### 4. CONCLUSION

This study investigates the effect of particles concentration and compatibilizer, on the thermal, mechanical and rheological properties of matrix HDPE filled with Nut-shells of Argan particles. The results show that tensile properties and stability of the composites are affected by particles concentration. The thermogravimetric analysis of NA particles and HDPE/ NA particles composite show two main behavior degradation stages. It is also noted that the content of residue is related to the content of the NA particles in the blends. Tensile properties are improved with the addition of PE-g-MA compatibilizer in HDPE/NA particles composites. The tensile properties are greatly influenced by increasing the filler in the matrix HDPE. The composite loses a lot of its ductility and toughness, but its rigidity increases. Rheological properties of HDPE/NA particles composites display non-Newtonian pseudoplastic shear thinning characteristic of the composite. Changes in complex viscosity, loss and storage modulus are not significant in the composite at 15 wt.% particles reinforcement with and without compatibilizer. The crossover point of the filled matrix is higher than the virgin matrix indicating that at higher frequency the transformation from solid like to liquid like is very fast.

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