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Thermal, mechanical and morphological properties of Nut-shells of Argan /PP composites treated with MAPP

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Abstract: This article presents the thermal, mechanical and morphological properties of Nut-shells of Argan/PP composites compared with Talc/PP composites. The effect of content, particles size and MAPP as coupling agent (5 wt.%) on the thermal, mechanical and morphological properties of the composites were also investigated. Thermal degradation takes place in three steps. In the first step, the composites and the matrix have a similar stability. In the second step, the matrix shows a slightly better stability than the composites. In the last step, the composites show a better stability than the matrix. But, the particles size has no significant effect on the thermal degradation of the composites. The experimental results reveal that the tensile strength tended to decrease with increasing NA particles size and content. Tensile modulus shows an increasing trend with increase in particle content. The morphological properties of surface were studied using Scanning Electron Microscope (SEM).

Keywords: Composites, polypropylene, Nut-shells of Argan, particles size.

Introduction

In recent years, there has been a development of the composites consisting of a thermoplastic matrix and reinforcement or filler from the natural and renewable resources such as Kenaf [1,4], hemp [2], jute [3], wood flour [14], bark [18], almond husk [16], walnut shell [5], apricot shell [6], rice husk [19]. However, the fillers from organic and renewable resources have become a strong competitor to inorganic fillers due to the fact that the first type have low densities, very low weight and cost, recyclability, high quantity of the filler, biodegradability, non-abrasiveness, and renewable nature [7, 8, 17]. Incompatibility and poor interfacial adhesion between the hydrophobic matrix and hydrophilic filler are usually the obstacle to the natural filler and polymer composites [9]. This defect affects the mechanical and thermal properties of biocomposite. It can be improved in several ways either by suitable selection of the thermoplastic matrix, or by optimising the interface between the filler and matrix through the use of coupling agents, and/or compatibilizer and/or sizes [20], or by optimising the filler-related properties such as filler content, particle size and dispersion [16, 19].

Social and environmental concern is the reason of the growing interest in renewable resources based products. Nut-shells of Arganis one of the major residues after Argan oils production which seasonally are accumulated in large volumes, approximately 130000 tons of waste in kingdom of Morocco. Nut-shells of Argan have several advantages, such as being inexpensive, with lower density, renewable and their disposal causing minor ecological impact. Nut-shells of Argan have no economical value or industrial usage in Morocco and generally are used only in the field of the combustion at home. But this way of utilisation of Nut-shells of Argan gives them no value. The prices of the other fillers from renewable sources have been steadily increased. For this reason, the Nut-shells of Argan produced in massive quantities by cooperatives and associations of production of Argan oil can play a significant role in the manufacture of filled thermoplastic matrix, which contribute to alleviating the demand of fillers from renewable resources.

A study has investigated the use of NA particle as reinforcement in polypropylene matrix [21], however the conclusion was that the interfacial adhesion was poor. To improve the adhesion and wettability between the filler and the polymer another coupling agent MAPP was used.

The objective of this work is to develop composite materials derived from environmentally friendly materials. This work investigates the effects of the coupling agent (MAPP), the particles sizes and content on the mechanical and thermal properties of polypropylene/NA particle composite. In order to situate the composite filled with the NA particles among the composites filled with the conventional fillers, a comparison was made with widely used talc filled PP composites.

Materials and methods

A. *Materials*

The particles of Nut-shells of Argan (NA) used in this work are from rural areas of southern west Morocco. The polymer matrix is polypropylene (PP), its melting temperature is 161°C, a density of 0,724 g /cm3 (240°C), and a melt flow index of 15,6 g/10 min (240 °C). The coupling agent is a maleic anhydride grafted polypropylene, its melting point is 167 °C, a density of 0,79 g /cm3 (240°C), and a melt flow index of 40,32 g/10 min (240 °C). The amount of the coupling agent used is 5% of the total weight of the composite.This amount was found optimal to enhanced the interfacial adhesion between the particle and the polymer matrix. The previously dried Nut-shells of Argan were ground into particles form. The particles were sieved and dried at 105°C for 24 h to adjust it to a moisture content of 2–3% and then stored in polyethylene bags.

B. *Methods*

- ***Preparation of composites***

Particles of Nut-shells of Argan/PP composites were prepared by Brabender type mixer (Brabender 350/EH equipped with rotors) at an angular speed of 70 RPM and an estimated temperature of 180°C below the degradation temperature of Nut-shells of Argan particles which is approximately240°C. Firstly, the Matrix is introduced and mixed for 2 min. Secondly, the coupling agent is introduced and mixed with matrix PP for 3 minutes which ensured a complete fusion of the polymer blend. Finally, the powder of NA particles is introduced after determining its percentage by weight and mix the blend for 5 min.For the manufacture of tensile test specimens apress (Dragon) was used. The first composite material is pressed into a hollow mold unders quare shape (10cm, 10cm)at a temperatureof140 °C and reached a pressure up to 150barfor 5 minutes. After the press until cooled to room temperature, a square plate shape is obtained. Then, to obtain the specimens, the plate was placed on a hollow dumbbell shaped mold between the two plates of the press at 140 °C for 5 min, after pressing the mold the hollow dumbbell shaped specimens are obtained. Similarly the test pieces of other formulations are obtained.

- ***Particles size measurement***

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

- ***Thermal analysis***

Thermal behavior was studied using a DTG-60 analyzer supplied by Shimadzu Company (Japan). Samples of 10-12 mg of the materials were placed in an aluminum pan and then heated from ambient temperature to 600°C at a heating rate of 10°C/min in air atmosphere.

- ***Tensile test***

Tensile testing is performed on an Instron 4466 machine, according to ASTM D 638. The specimens were tested at crosshead speed of 5 mm/min at room temperature. All the reported values for the tests were the average values of five specimens.

- ***Scanning Electron Microscope (SEM)***

The surface morphology of tensile specimens was investigated using a scanning electron microscope, Hitachi S4700.

Results and discussion

A. *Particles size of Nut-shells of Argan*

Figure 1 illustrates the particles size distribution curve of Nut-shells of Argan particles acquired from the particles size analyser. The average size of the NA particles was 68.33 µm.

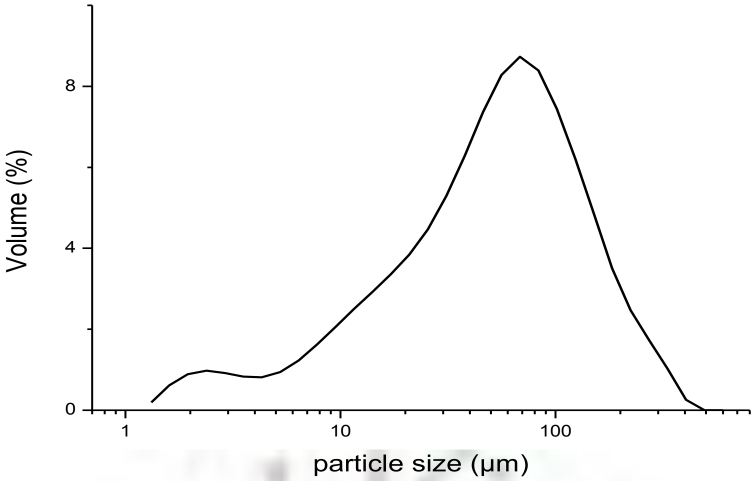


Figure 1: Particles size distribution curve for Nut-shells of Argan.

B. ***Thermal stability***

- ***The effect of content on degradation of PP and NA particles composites***

Thermogravimetric analysis allows toinvestigate the thermal stability and thermal decomposition of PP/NA particles composites. Figure 2 shows the TGA and DTA of the pure PP matrix and the effect of NA particles content on the thermal stability of the matrix.

According to figure 2 (a), in case of NA particles decomposition curve shows three mass loss steps. The first mass loss step, in the temperature range 70-150°C, corresponds to the weight loss of almost 8,5% due to the moisture drying. The second mass loss step occurs at the temperature range of 250-350°C corresponds to the degradation of the major constituents of NA particles such as cellulose, hemicellulose and lignin (mass loss 52%). The third step is attributed to oxidative degradation of the charred residue. The weight loss of PP takes place at the temperature ranged from 260°C to 415°C. Above this last temperature, the polymer is completely transformed to the gaseous state. For the PP/NA particles composites brings together both cases above. The decomposition of the composite is in three steps. The first step corresponds to the degradation of organic constituents and evaporation of the moisture. In this step, the weight loss of the composite increases with increasing of NA particles content on the composite while the second step is associated to degradation of the pure polypropylene, but the temperature of degradation decreases by raising the loading rate (20°C for 30wt%). The last temperature range corresponds to the degradation of the carbon. In addition, the yielded char of the PP/NA particles composites increases with increasing NA particles contents. The yielded char of the composite with a filler raised from 10wt% to 30wt% NA particle contents were increasing from 3.6wt% to 10.6wt% respectively. The thermal stability of PP/NA particles composites decreases with increasing NA particles contents compared to pure polymer.

Figure 2 (b) shows the differential thermal analysis of NA particles, polypropylene and PP/NA particles composite. The DTA thermogram shows that NA particles exhibited three peaks. The first endotherms peak is at 70°C which is attributed to evaporation of water. The second main exotherm peak is at 320°C is due to degradation of NA particles main constituents and is probably due to the decomposition of cellulose, this is ascribed to rapid volatility of degradation products leading to formation of volatile products [10, 11, 12]. The third main exotherm peak is at 468°C which is probably due to the oxidation of volatile and charred products [10, 13]. The DTA thermogram of the polypropylene shows three peaks. The first endotherm peak is at 170°C, which can be attributed to the melting point of the polymer. This endotherm is followed by a second exotherm peak is at 268°C and a third endotherm peak is at 422°C which corresponds to the decomposition of the polymer. For the DTA thermograms of the PP/NA particles composites with a different content show that when the filler content is increased, the peaks of the decompositions of composite constituents move toward the lower temperature. Introducing the filler NA particles in the polypropylene matrix decreases its stability. This is attributed to the thermal stability of NA particles less than that of the polymer and the high shearing and frictional forces that occur between the particles and the polypropylene matrix during mixing are thought to have caused breakage of the polypropylene polymeric chains, due to the high hardness of NA particles [10].

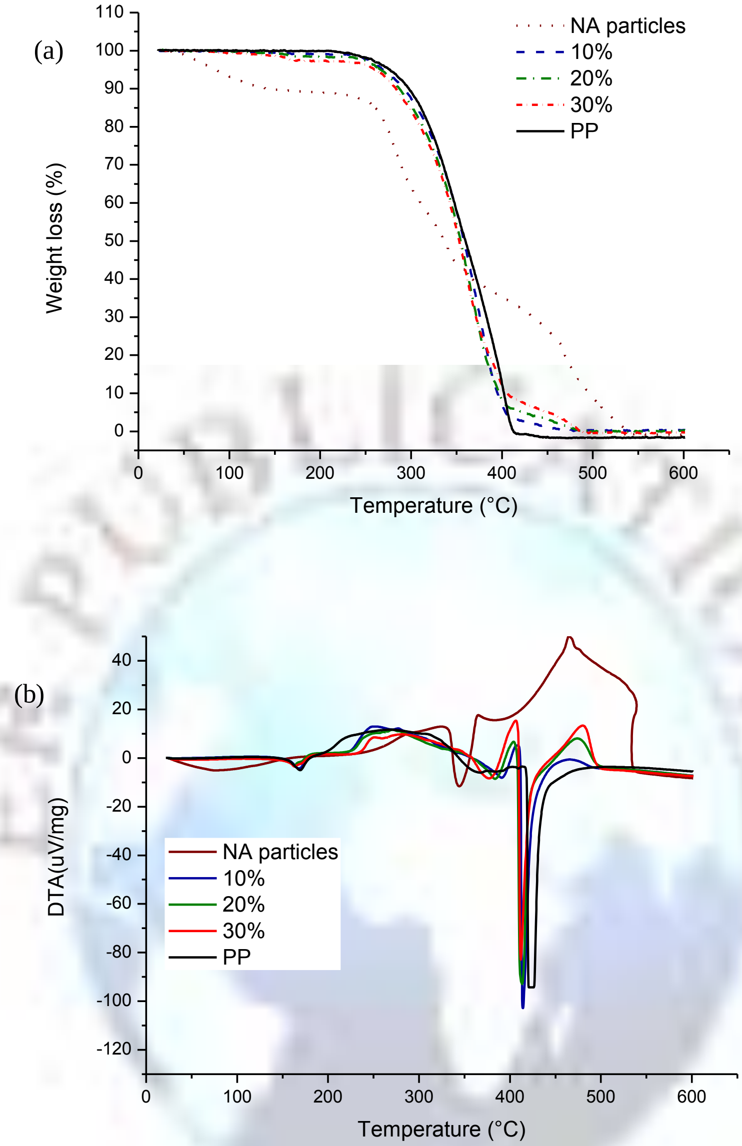


Figure 2 : the effect of NA particles content on TGA and DTA of PP/NA particles composites.

- ***The effect of particles size on degradation of PP and NA particles composites***

Figure 3 (a) shows the TGA curves of NA particles, PP with 5% of MAPP and PP/NA particles with different particles sizes. The PP/NA particles with 5% p MAPP composites are less thermally stable than PP. Increased particles size leads to a decrease of the thermal stability of the composite below that of pure PP, and always three decomposition steps can be seen for a loading content by weight of 20% of NA particles. This can be due to weak interfacial interaction between polymer and filler and to the high content of NA particles, which leaves NA particles agglomerate and are not in intimate contact with PP, which does not preserve the particles against the heat, knowing that these last degrades before the rest of the composite. Comparing the stability of the composite filled of the different NA particles sizes shows that they do not have significant influence on the thermal stability of the composite, but the polymer loaded by NA particles more than 100µm becomes less stable than other composites that have almost the same stability.

Figure 3 (b) plots the differential thermal analysis of PP/NA particles composites with different particles sizes. The DTA curves of PP/NA particles composites filled with different powders with particles sizes less than 100µm show that there is almost no effect on the thermal stability of the composites. But it always remains lower than that of the polypropylene matrix. Whereas, the DTA curve of the composite filled by powders having particles size greater than 100µm shows a slight decrease in temperature peaks to the low temperatures. This can be attributed to the presence of less particles than the other composites in the same matrix ratio [14]. So we see that the particles size has an effect on the loss of the mass of the heat treated samples.

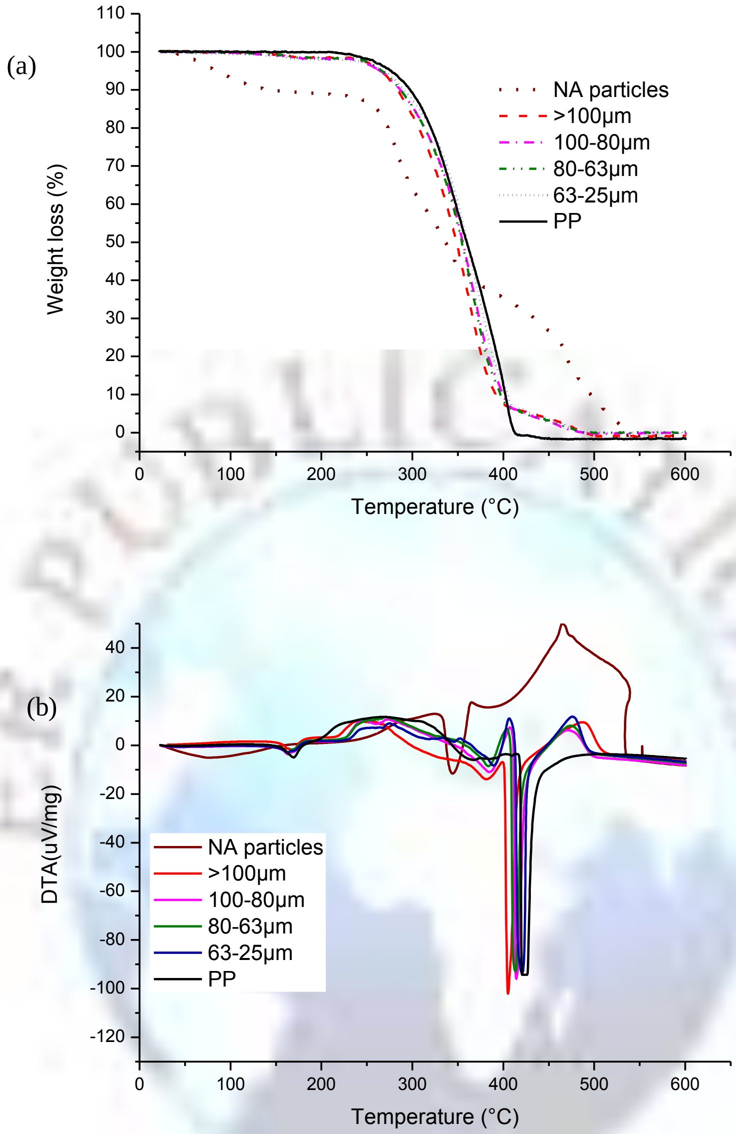


Figure 3: the effect of NA particles sizes on TGA and DTA of PP/NA particles composites.

- ***Comparison ofdegradation of NA particles and Talc filled PP composites***

Figure 4 (a) plots the comparison of the thermal stability and the weight content of the residue of PP, PP/ NA particles composite (filler content: 10 wt.%) and PP/ Talc composite (filler content : 10 wt.%). The thermal stability of the composite filled with NA particles is higher than that of the composite filled with talc due to a decreasing temperature of degradation of polymer. However, the thermal stability of PP/talc composite at high temperatures increases more than the stability of composite filled with NA particles. It can be seen that the weight content (9.6wt.%) of the residue is higher for Talc filled composite, almost the same content added at the beginning even if the temperature exceeds 600°C. On the contrary, we find that the composite filled with NA particles is totally disappeared at temperature of 470°C.

Figure 4 (b) plots the differential thermal analysis of PP/NA particles composite, PP/Talc composite and polypropylene. The DTA curves show that there are no significant changes in the temperature in the first endothermic peak and exothermic peak, but for the temperature in the second endothermic peak of the polypropylene filled with NA particle is greater than that of the polypropylene filled with Talc. The temperature peak of PP/Talc composite compared to neat PP decreases by 24°C and it decreases by 16°C compared to PP/NA particles composite. Which makes the composite loaded with organic filler more thermally stable than that loaded with inorganic filler.Which confirms the thermogravimetric analysis.

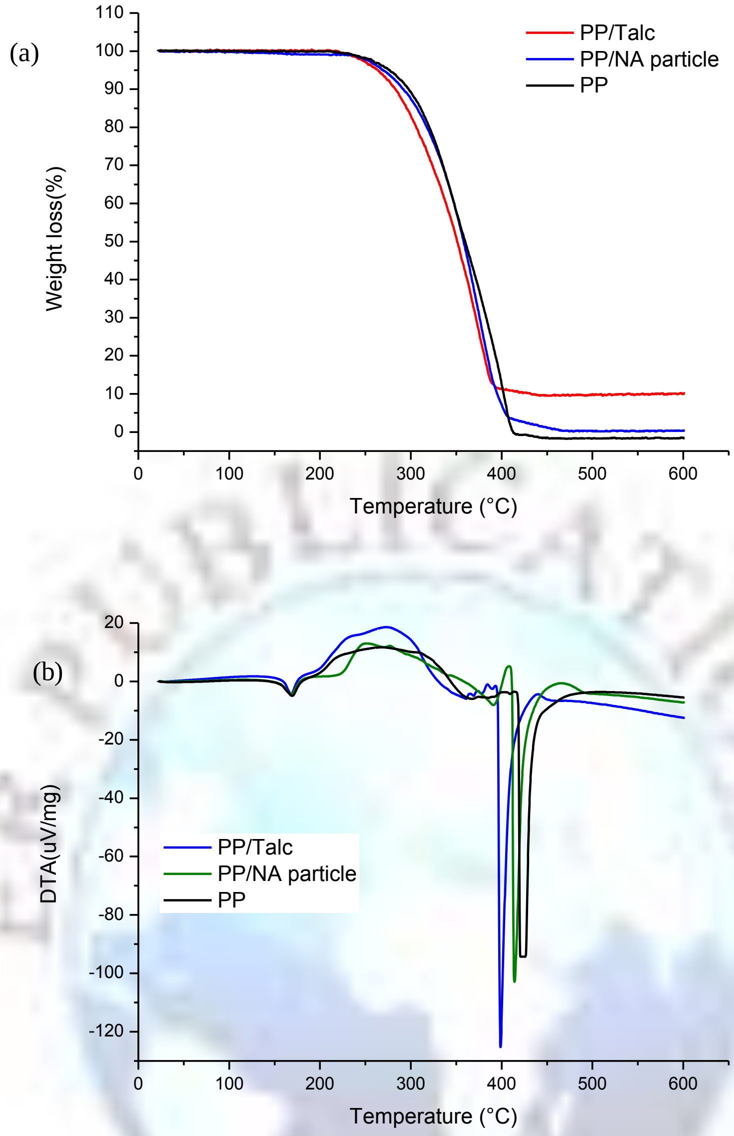


Figure 4: Comparison between ATG and DTA curves of PP, PP/NA particles and PP/Talc powder composite filled of 0%, 10%, 10% by weight respectively.

C. *Tensile Properties*

- ***The effect of the particles content***

Figure 5 (a) shows the stress-strain behavior of polypropylene and PP/NA particles composites with the filler content of 5%, 10%, 20% and 30%. The curves show that PP can be elongated more than 30% without breaking, allowing us to distinguish different areas of the plastic domain: stress whitening followed by necking then area stretching and when it reaches the final hardening, it breaks. For the curves of PP/NA particles composite, the stress increases linearly with the increase of the strain for all samples, but when it reaches the end of the plastic zone for definite value of the stress, the curves show a nonlinear behavior. With the addition of NA particles to matrix the transition from ductile to quasibrittleoccurs. Furthermore, when the filler content is increased, the samples rupture occurs at the lowest strain rate.

Figure 5 (b) shows the effect of the filler (NA particles) content on the tensile strength, tensile modulus and strain of the composite particles of 25-63 µm size. It can be seen that the tensile strength values decrease and the tensile modulus increase as the filler concentration increases. This decrease in tensile strength is attributed to the poor PP/NA particles interfacial bonding, which leads to the increase of interfacial defects, which leads to the concentration of stresses around the filler particles. Good tensile strength depends more on effective and uniform stress distribution. Having said that, we can deduce that the particles do not work as carriers of stress in the matrix. This explains the decrease in tensile strength.

For the tensile modulus, it increases from 0.786 Gpa to 1.137 Gpa when the content of filler increases from 0% to 30% respectively. It can be attributed to the increase of filler content which has a higher stiffness than the PP polymer. This may be due to the increase in filler content which leads to a higher surface area of NA particles. When the surface area is increased, the filler-matrix adhesion is improved resulting in decrease in mobility of macromolecules. Similar behavior has been reported by several authors with different filler [15, 16, 17,18]. The tensile strain is 500%, 10%, 9%, 6% and 3% for 0%, 5%, 10%, 20% and 30% filler content respectively. The lowest elongation at break of NA particles and its brittleness can be the reason of the decrease in strain with increase in filler content. This decrease of strain can also be explained by reduction of the ability of the samples to deform in presence of NA particles by restricting the mobility of polymer chains. As a consequence, it is difficult for the segments of the material to easily slip away from each other.

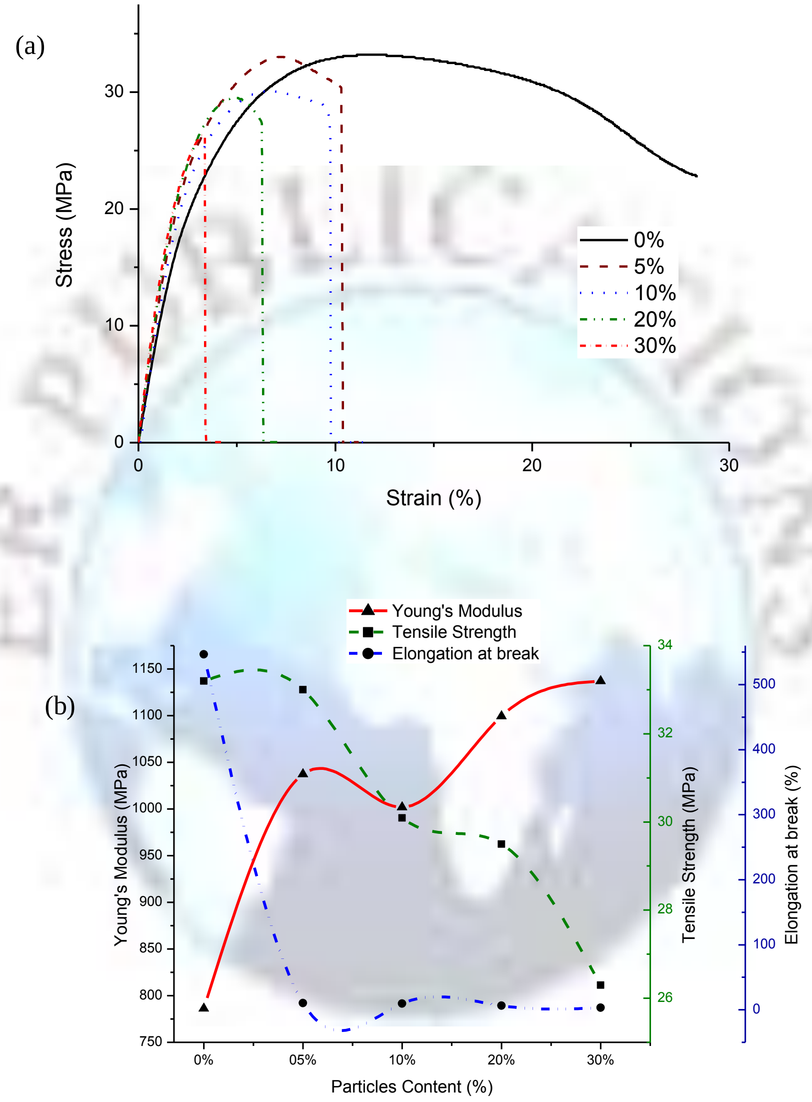


Figure 5: the effect of NA particles content on mechanical properties of PP/NA particles composites

- ***The effect of the particles size***

Figure 6 (a) plots the stress-strain behavior of PP and PP/NA particles composites filled with 20% by weight of the particles. These particles having diameter intervals <25µm, 25-63µm, 63-80µm, 80-100µm and >100µm. The curves show that the stress increases linearly with the increase of the strain. The samples filled with particles size lower than 100µm have the same tendency, while that sample whose diameter is more than 100µm the tendency of the curve decreases. We note that the tendency of the curve is affected by the particlessize. The curves show nonlinear behavior when the strain is above the plastic zone. Furthermore, it can be seen that the breaking of samples occurs at a lower strain rate when particles size increase.

Figure 6 (b) shows the effect of particles size on the tensile strength, tensile modulus and strain of the composites. The curve shows that the tensile strength decreases with the increasing of the particles size. This can be attributed to good dispersion of smaller particles in the composite and larger particles of NA tend to induce large cavities in the interface, resulting in interfacial defects or debonding between matrix and NA particles [19]. The curve of the tensile modulus shows that there is almost no notable change in the modulus, but when particles size becomes greater than 100 µm, we can see a dramatic decrease in the tensile modulus. This can be due to better reinforcing action of the smaller particles and better distribution inside polymer of the particles of smaller size, which provides materials with a bigger homogeneity than materials with particles with higher size. This may be due to the higher surface area of the filler with a smaller particles size than that of the filler with a larger particles size. When the surface area is increased, filler-matrix adhesion is improved resulting in a decrease in mobility of the macromolecules [16, 17]. For the curve of the strain shows that there is a slight decrease in elongation at break with increasing particles size. This may be attributed to the uniform distribution of NA particles having a lower size [15].

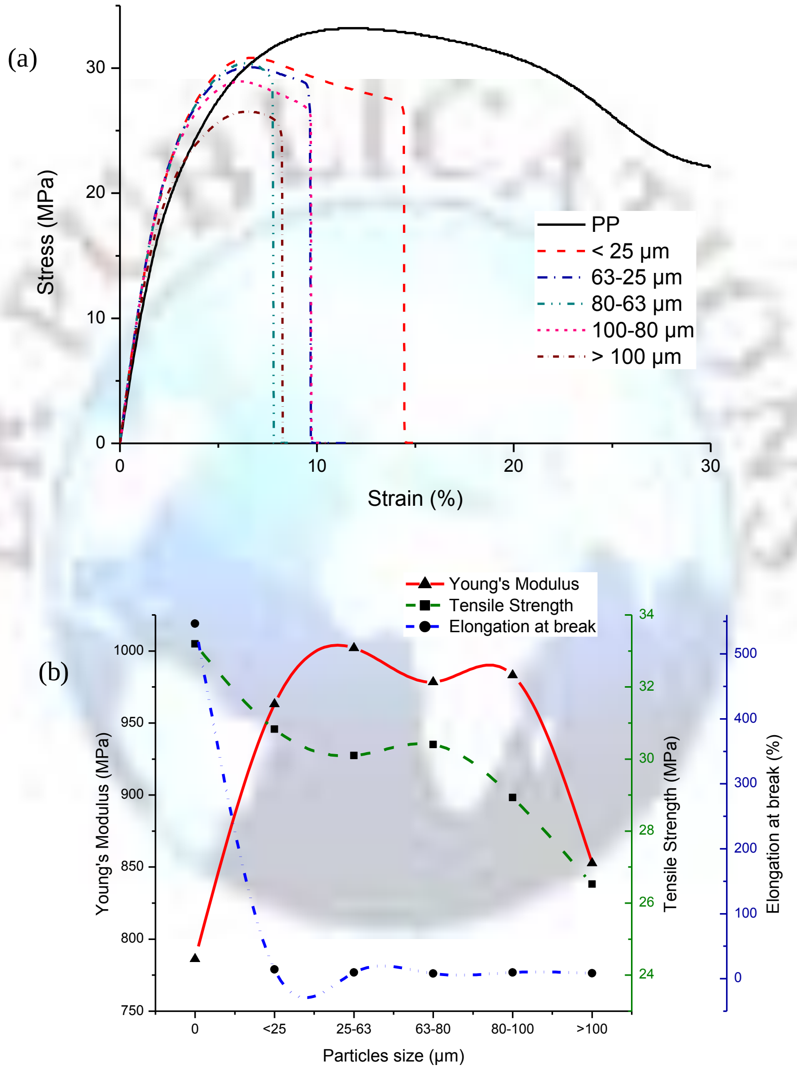


Figure 6: the effect of NA particles sizes on mechanical properties of PP/NA particles composite

- ***Comparison of NA particles and Talc filled PP composites***

Figure 7 shows the stress-strain behavior of polypropylene and NA particles and Talc filled PP composites with the filler content of 10%. The curves show that PP can be elongated more than 30% without breaking. For the curves of PP/NA particles composite, the stress increases linearly with the increase of the strain, but when it reaches the end of the plastic zone for definite value of the stress, the curves show a nonlinear behavior. The same behavior can be seen for the composite filled with Talc. When NA particles are added to the matrix, the transition from ductile to quasibrittle occurs and it is more than that of the composite filled with Talc. Furthermore, the samples rupture of the composite filled of NA particles occurs at the lowest strain rate than that of the composite filled of Talc.

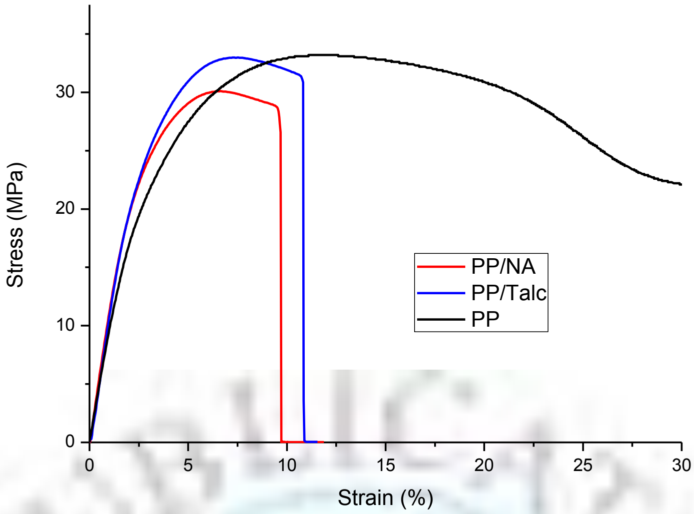


Figure 7: Comparison between Stress-Strain curves of PP, PP/NA particles and PP/Talc powder composite filled of 0%, 10%, 10% by weight respectively.

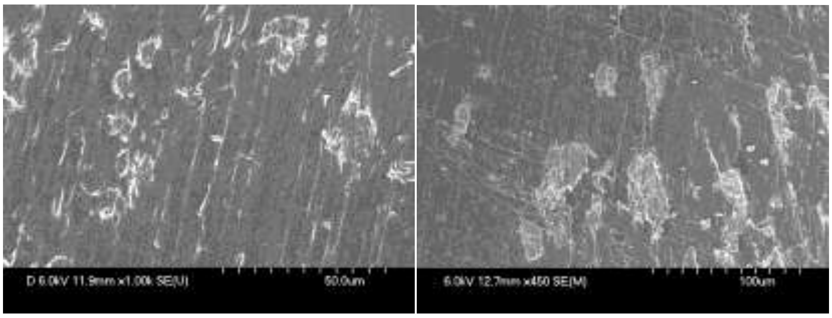
Table 1 shows the tensile properties of PP and NA particles and Talc filled PP composites. The comparison of young modulus of the PP and the composites shows that the young modulus of the composites are higher than that of pure PP. the tensile modulus of the PP filled with talc is slightly higher than the modulus of PP filled with NA particles. This can be due to the smaller particles size of talc, which gives higher surface area than that of NA particles. This enhances the surface adhesion between the particles and matrix which is attributed to a decrease in mobility of macromolecules. The comparison of the tensile strength shows a slight decrease in the tensile strength of the composites compared to that of the pure PP. But, the decrease of the tensile strength of the matrix PP filled of NA particles is more than that filled with Talc which can be due to the good dispersion of the particles of Talc in the matrix PP than that of NA particles. This forms more agglomerates of NA particles in the matrix than talc. These agglomerates produce the cavities in the composite which leads to the concentration of stress. These factors are attributed to lower tensile strength of PP/NA particles composite compared to that of PP/Talc composite. The incorporation of the fillers in the matrix PP result higher decrease on the elongation at break of the composites compared to the elongation at break of the pure matrix PP. It is seen that PP/NA particles composite have less elongation at break than PP/Talc composite, but the difference is not significant.

Table 1: Tensile mechanical properties of PP filled with NA particles and Talc composites.

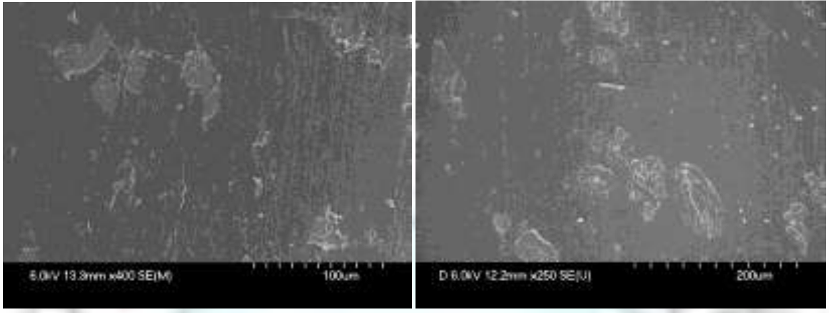
Composites	Young'smodulus (MPa)	Tensilestrength (MPa)	strain (%)
PP	786.25	33.20	>30
PP/NA (90/10)	1008	30.08	9.71
PP/Talc (90/10)	1009.7	32.98	10.85

D. *Scanning electron microscopy*

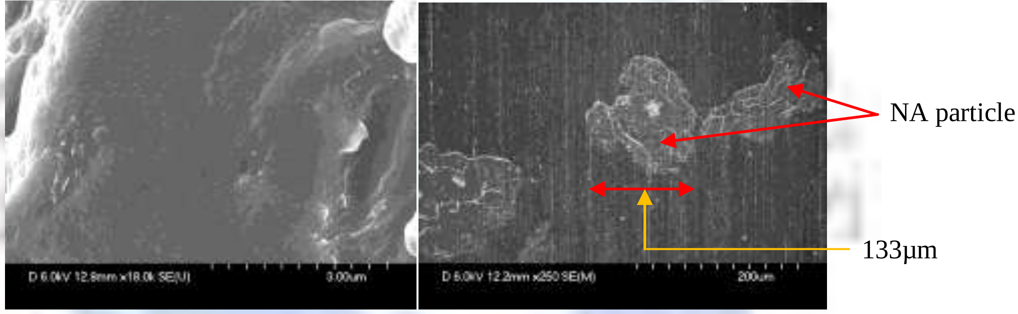
Figure 8 shows the dispersion of NA particles in the PP matrix (10 wt.%) and the interfacial adhesion between the NA particles PP matrix polymeric. The dispersion and adhesion are studied by using scanning electron microscopy (SEM). The particles of the Nut-shells of Argan appears to be almost free of any matrix material adhering to them, indicating a poor interfacial adhesion between the polymeric matrix PP and the filler of NA particles. For NA particles having lower size is well dispersed and most of the particles surfaces are covered with the matrix material attesting for adequate compatibility between the two phases. This results in less cavities and agglomeration in the composite. These are clear morphological clues supporting the increase in the tensile strength and the tensile elongation at break compared to composites with higher particles size. Besides, it can be observed that the large size of NA particles cause greater cavities and lead to the larger defects created within the samples. This can explain the lowering of the tensile modulus and the tensile strength compared to the matrix PP filled with lower NA particles size.



(a) <25 µm (b) 63-25µm



(c) 80-63 µm (d) 100-80µm



(e) >100 µm

Figure 8 : Morphology of the PP/NA particles composites (10 wt.%) with various NA particles size. (a) <25 µm, (b) 63-25 µm, (c) 80-63 µm, (d) 100-80µm, (e) >100 µm.

Conclusion/Results

From this study, we can conclude that the Thermal degradation takes place in three steps: in the first step, the composites as well as the matrix have similar stability. In the second step, the matrix shows slightly better stability than the composites. In the last step, composites show better stability than the matrix. But, there is no effect of particles size on the thermal stability. The tensile strength and strain decrease with the increase of the content and particles size. The tensile modulus increase with the increase in particles content and particles size. However, PP/Talc composite show higher tensile strength and slight increase on the both of the tensile modulus and the strain compared to PP/NA particles composite. The morphological observations show that the adhesion between the matrix and the particles is affected by particles size. When the particles size increases, a poor adhesion is obtained.

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