



## Investigation of Mechanical Properties Prediction of Synthesized Nylon-66/Nano-Calcium Carbonate Composites

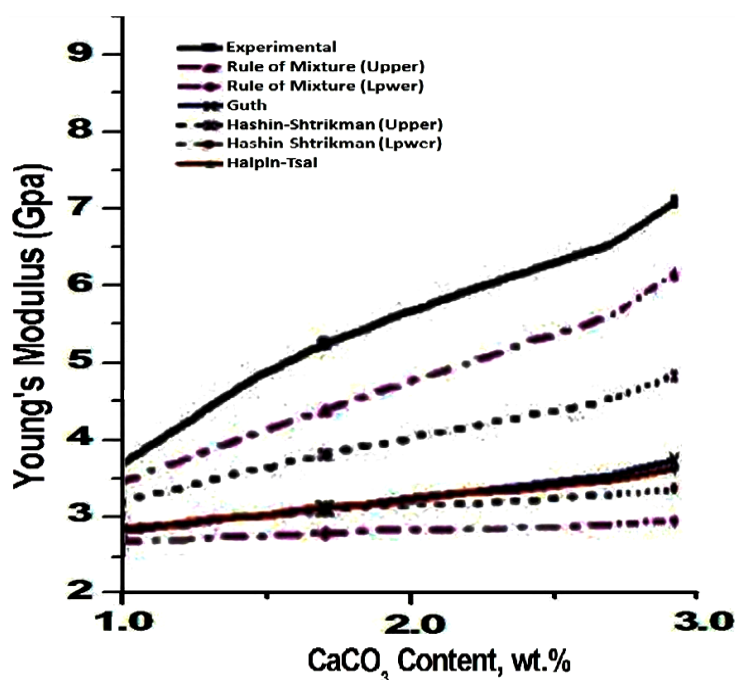
Aboutaleb Ghadami Jadval Ghadam

Departments of Chemical & Petroleum Engineering, Yasooj Branch, Islamic Azad University, Yasooj, I.R. Iran

### HIGHLIGHTS

- Nano-CaCO<sub>3</sub> particles were synthesized using microemulsion method with an average size of 33nm.
- It was observed that tensile strength and young's modulus increased and elongation decreased with increasing CaCO<sub>3</sub> particles in the composites.
- The used models can be used with confidence for the prediction of elastic modulus.

### GRAPHICAL ABSTRACT



### ARTICLE INFO

#### Article history:

Received 12 May 2016  
Received in revised form  
15 June 2016  
Accepted 24 June 2016

#### Keywords:

Additives  
Nylon-66  
CaCO<sub>3</sub> particles  
Composites  
Mechanical properties  
Rule of mixtures

### ABSTRACT

In this research, the influence of adding micro- and nano- sized calcium carbonate powders to nylon-66 was investigated. Mechanical properties of micro and nano-composites, including tensile strength, elongation, and Young's modulus, before and after ageing, were determined and analyzed. For this purpose, micro- and nano-sized CaCO<sub>3</sub> particles were used as fillers to prepare micro-composites (conventional composites) and nano-composites via a polymer solution method. It was observed that tensile strength and young's modulus increased and elongation decreased with increasing CaCO<sub>3</sub> particles in the composites. Also, nano-composites had higher strength and modulus than micro-composites. Theoretical prediction of elastic modulus was carried out using rule of mixtures, Guth, Nicolais–Narkis, Hashin–Shtrikman, and Halpin–Tsai equations. Calculated results show that these equations are not suitable for accurate prediction for the work carried out. However, these models can be used with confidence for the prediction of elastic modulus because experimental results are higher than the calculated values.

## 1. Introduction

Polymer composites represent an important class of engineering materials. The incorporation of inorganic fillers into thermoplastics has been widely practiced in industry to extend them and to improve certain properties. One primary purpose of adding inorganic fillers to polymers is cost reduction [1]. The mechanical reinforcement of engineering polymers with micro- and nano-fillers also plays an important role in the plastic industries. The performance of these materials will however be highly dependent on factors relating to the intrinsic characteristics of the materials and factors relating to the process. The intrinsic factors primarily include the aspect ratio of the filler, surface chemistry, and surface polarity and filler–matrix interfacial properties. Often, the structure–property–process relationships in nano-composites are complex. Experimentals have shown that nano-scale reinforcement brings new phenomena, which contributes to material properties [2, 3]. For this work, the nanosized inclusions are defined at those that have at least a dimension in the range of 1–100 nm. One of the most common fillers with long history of applications in various fields is  $\text{CaCO}_3$ . It has been used in plastics, paint, paper, inks, food as well as pharmaceutical industries [4]. It is pertinent to put on record that calcium carbonate ( $\text{CaCO}_3$ ) has been one of commonly used inorganic fillers for thermoplastics such as PVC and PP. Micron-sized  $\text{CaCO}_3$  is historically used to lower the cost of relatively expensive polymer resins. The results of numerous studies have indicated that the improvement in the mechanical properties of micron-sized  $\text{CaCO}_3$  filled composites is found to be minimum [5]. It may be due to poor particle–polymer interaction [6]. It is well-known that the dispersion of a filler in the polymer matrix can have a significant effect on the mechanical properties of composites [2, 6]. The dispersion of an inorganic filler in a thermoplastic is not an easy process. A good dispersion can be achieved by surface modification of the filler particles and appropriate processing conditions. Many efforts have been devoted to surface-modified  $\text{CaCO}_3$  filler to increase the interaction between the polymer and filler. The effects of surface modification on mechanical properties have been positive. The use of nano-sized  $\text{CaCO}_3$  particles may bring new insights in the study of polymer inorganic nano-composites. In addition, when surface smoothness and high gloss are required micron-sized  $\text{CaCO}_3$  cannot be used. Nano- $\text{CaCO}_3$  particles can be good filler that can provide surface smoothness and high gloss [6]. Nylon-66 (PA66) is a semi-crystalline material that has a combination of strength, flexibility, toughness, and

abrasion resistance. It is also known for its dye-ability, low coefficient of friction (self-lubricating), low creep, and resistance to solvents, oils, bases, fungi, and body fluids. The applications of nylon-66 range from textile fibers, membranes, tapes, food packaging to electronics and automotive parts [7]. Making good samples of polymers matrix nano-composites are a challenging area that draws considerable effort. Researchers have tried a variety of processing techniques to make polymer matrix nano-composites. These include melt mixing, in situ polymerization, sol–gel process, polymer solution method, and other approaches. Creating a universal technique for making polymer nano-composites is difficult because of the physical and chemical differences between each system and various types of equipment available to researchers. Each polymeric system requires a special set of processing conditions to be formed, based on the processing efficiency and desired product properties. So, the different processing techniques in general do not yield equivalent results [8].

The present study aims to prepare nylon-66/ $\text{CaCO}_3$  micro- and nano-composite through polymer solution method while the micro-particles (procured in the lab) and nano-particles of  $\text{CaCO}_3$  [9] were used as filler. The characteristics and properties of the two composites (micro and nano) have been compared. The mechanical properties (tensile tests) of composites at room temperature were measured by Universal Testing Machine (UTM) according to ASTM-D882. In order to predict tensile properties of synthesized micro- and nano-composite samples, some theoretical models i.e. the Mixture rule, Nicolais-Narkis theory, Guth's equation, Hashin-Shtrikman model, and Halpin-Tsai model, were used and results were compared with experimental data.

## 2. Theoretical

The field of composites material behavior can be studied from two points of view namely, micromechanics and macromechanics. Micromechanics analyze composite behavior by studying the interaction between constituent materials. Whereas, macromechanics studies composite behavior by assuming the body is homogeneous and the effects of the constituent materials are detected only as averaged properties of the composite [10]. The mechanism for nano-sized particles and nylon matrix interface is a feature that so far no clear mechanism presented in the literature, to relate mechanical properties to interface nature of nano-composite. Studying interface of nano-composite is still edge of science and so far no unique mechanism is developed.

The aim of most micromechanics approaches is to determine the elastic moduli or stiffness of a composite material in terms of the elastic properties of the constituent materials. Most of the analytical models presented presume the idealization that there is perfect adhesion between the phases and that the particles are spherical and evenly dispersed. These theories therefore predict that the properties of composite materials are independent of the size of particles. In general, this is correct for systems with micron-sized reinforcements, but may not be true for nanocomposite systems. In the past few years, a considerable amount of research has been conducted to examine the modeling of mechanical properties of polymer composites with nanoscale reinforcement. Some of the earlier attempts in modeling composites were performed by Einstein and Guth. Guth and Smallwood extended Einstein's theory to explain rubber reinforcement [1]. Both of these attempts have proved to be applicable. Thus, the focus will be on the newer works, separated into two approaches, defined as either mechanics of materials or an elasticity approach. In the mechanics of materials approach some simplifying assumptions are made,

the most significant of which is that the strain in the matrix is equal to the strain in the particulate. With this assumption the most simplistic of all methods of predicting the moduli of a composite, known as the rule of mixtures, can be obtained from Equation-1 [6, 10-11].

$$E_c = E_f \varphi_f + E_p \varphi_p \quad (1)$$

Where,  $E_c$ ,  $E_f$  and  $E_p$  are the elastic modulus of compound, filler and polymer matrix, respectively.  $\varphi$  is the volume fraction, subscript p denotes the matrix of continuous phase, polymer, and subscript f denotes the particulate or filler phase.

In general, the rule of mixtures is regarded as the upper limit of the elastic modulus. The absolute lower bound on elastic modulus can be obtained assuming equal stress in the matrix and particulate, Equation-2:

$$E_c = \frac{1}{\frac{\phi_f}{E_f} + \frac{\phi_p}{E_p}} \quad (2)$$

The upper and lower limits on elastic moduli represent the widest relationships produced from the mechanics of materials approach. Most of the attention has been given to the elasticity approaches.

Lower bound:

$$E^l = \frac{9K^l G^l}{3K^l + G^l} = \frac{9 \left[ k_1 + \frac{\phi_2}{\frac{1}{k_2 - k_1} + \frac{3\phi_1}{3k_1 + 4G_1}} \right] \left[ G_1 + \frac{\phi_2}{\frac{1}{G_2 - G_1} + \frac{6(k_1 + 2G_1)\phi_1}{5G_1(3k_1 + 4G_1)}} \right]}{3 \left[ k_1 + \frac{\phi_2}{\frac{1}{k_2 - k_1} + \frac{3\phi_1}{3k_1 + 4G_1}} \right] + \left[ G_1 + \frac{\phi_2}{\frac{1}{G_2 - G_1} + \frac{6(k_1 + 2G_1)\phi_1}{5G_1(3k_1 + 4G_1)}} \right]} \quad (3)$$

The composite spheres model introduced by Hashin consists of a graduation of sizes of spherical particles fixed in a continuous matrix phase. In line with this model Hashin and Shtrikman developed the bounds for the shear and bulk modulus. The resulting bounds on the Young's modulus are shown in Equations-3 and 4 [10, 12].

Upper bound:

$$E^u = \frac{9K^u G^u}{3K^u + G^u} = \frac{9 \left[ k_2 + \frac{\phi_1}{\frac{1}{k_1 - k_2} + \frac{3\phi_2}{3k_2 + 4G_2}} \right] \left[ G_2 + \frac{\phi_1}{\frac{1}{G_1 - G_2} + \frac{6(k_1 + 2G_1)\phi_1}{5G_2(3k_2 + 4G_2)}} \right]}{3 \left[ k_2 + \frac{\phi_1}{\frac{1}{k_1 - k_2} + \frac{3\phi_2}{3k_2 + 4G_2}} \right] + \left[ G_2 + \frac{\phi_1}{\frac{1}{G_1 - G_2} + \frac{6(k_1 + 2G_1)\phi_1}{5G_2(3k_2 + 4G_2)}} \right]} \quad (4)$$

In the above equations,  $K^l$ ,  $K^u$ ,  $G^l$  and  $G^u$  are lower bound for the Bulk moduli; the upper bound; the lower bound of the Shear moduli and corresponding upper bound, respectively. In addition, subscripts 1 and 2 refer to the polymer and the filler respectively. It may be worth mentioning that the above equations are applicable when  $K_1 < K_2$  and  $G_1 < G_2$  [10, 12]. The Halpin–Tsai semi-empirical equations represent yet another way to predict composite properties, Equations-5 and 6 [10, 13]

$$E = \frac{E_1(1 + \zeta\eta\phi_2)}{1 - \eta\phi_2} \quad (5)$$

where.

$$\eta = \frac{\frac{E_2}{E_1} - 1}{\frac{E_2}{E_1} + \zeta} \quad (6)$$

And  $\zeta = 2$  (for a first approximation). Some additional mechanical relationships are presented later for Young's modulus and the Poisson's ratio of a composite, as given by Busiansky, Equations 7–10 [10].

$$E = \frac{9KG}{3K + G} \quad (7)$$

$$\nu = \frac{3K - 2G}{6K + 2G} \quad (8)$$

and for each constituent

$$K_n = \frac{E_n}{3 - 6\nu_n} \quad (9)$$

$$G_n = \frac{E_n}{2 + 2\nu_n} \quad (10)$$

Where,  $n = 1$  or  $2$  (denoting continuous and filler phases respectively).

The modulus and yield strength of nanoparticle-filled composites also can be predicted respectively by Guth's equation, Equation-11 [14, 15].

$$E_c = E_m(1 + 2.5\phi_f + 14.1\phi_f^2) \quad (11)$$

and Nicolais–Narkis theory, Equation-12 [14].

$$\sigma_{yc} = \sigma_{ym}(1 - 1.21\phi_f^{2/3}) \quad (12)$$

Where,  $E$  and  $\sigma_y$  are Young's modulus and yield strength, respectively; subscripts  $m$ ,  $f$ , and  $c$  denote matrix, filler and composite, and  $\phi_f$  is volume fraction of particles.

### 3. Experimental

#### 3.1. Materials

CaCO<sub>3</sub> nano-particles with an average size of 33 nm were synthesized via microemulsion route [9]. CaCO<sub>3</sub> particles with an average size of 2 μm and Dimethyl Sulfoxide (DMSO), 99%, were procured from Merck Company, Germany. Injection molding grade Nylon-66 polymer from SRF Limited, India was used to produce the micro and nano-composites.

#### 3.2. Synthesis of Micro and Nano-Composites

Polymer solution method was used for the synthesis of micro and nano-composites. Effect of the quantity of micro and nano-particles of CaCO<sub>3</sub> on the synthesized composites was studied for 0, 1, 2 and 3 wt.%. For preparation of polyamide-66/CaCO<sub>3</sub> composites, Polyamide-66 (PA66), micro and nano- calcium carbonate particles were first heated in a vacuum oven for 12 hrs at 100°C until any possible residual moisture was removed. Then, polyamide-66 was dissolved in DMSO until a homogeneous solution was obtained. Different amounts of CaCO<sub>3</sub> particles were carefully added to this PA66 solution under vigorous stirring with a magnetic stirrer bar at room temperature (27°C). The stirring was carried out for 24 hrs under ambient condition of 27°C to get the proportion of 1, 2, and 3 wt.% of nano-sized CaCO<sub>3</sub> based on PA66 content. Subsequently, the resulting solution was poured onto clean glass plates with side tapes around the glass plates (acting as thin trays) and dried until tack-free in a low humidity chamber at room temperature. Then, the resultant films were vacuum dried for 24 hrs at 60°C until all the solvent was removed by evaporation and delivered polymer nano-composite. All films were prepared for the same time and ambient conditions. Pure PA66 films were prepared in the same manner which also showed opaqueness and milk-white color upon drying of solvent. Conventional composite films were also prepared in the same procedure containing 1, 2, and 3 wt.% of micro-sized CaCO<sub>3</sub>.

### 3.3. Filler Dispersion Analysis

The synthesized nano-calcium carbonate powders [9] were dispersed in isopropyl alcohol (IPA) and placed in an ultrasonic bath to ensure fine dispersion. Two to three drops were then placed on a filter paper and the  $\text{CaCO}_3$  nano-particles were observed under a Transmission Electron Microscope, TEM, (JEOL JEM-2100F, Japan) at 120 KV. The average primary particle size of the nano-particles was then determined from the TEM photomicrograph.

The phase morphology of the nylon-66/calcium carbonate nano-composites was examined using a Scanning Electron Microscope, SEM (SEM, Carl Zeiss: EVO40) at 20 kV. The samples were sputter-coated (Sputter Coater: POLARON-SC7640) with a thin layer (10–20 nm) of gold palladium. The coating was carried out by placing the specimen in a high vacuum evaporator and vaporizing the metal held in a heated tungsten basket.

### 3.4. Mechanical Properties Evaluation

Tensile strength, Young's modulus and percent elongation at yield and break were measured at room temperature according to ASTM-D882 [16] by Zwick 1445 Universal Testing Machine (UTM). The test specimen (film) dimension was  $7 \times 0.8 \times 0.09 \text{ cm}^3$  (*Length*  $\times$  *Width*  $\times$  *Thickness*). For each composite type, seven specimens were used and the average value of three replicated tests was taken for each composition. Subsequently, the mean values and their standard deviations were calculated. The test specimen gauge length was 5.1 cm and crosshead speed for the film testing was 0.10 cm/min.

### 3.5. Predicting Elastic Moduli

For the prediction of Young's modulus, rule of mixtures (Eqs. 1 and 2), Hashin–Shtrikman (Eqs. 3 and 4), Halpin–Tsai equations (Eqs. 5 and 6), Guth equation (Eq. 11), and Nicolais–Narkis theory (Eq. 12), were used. The Young's modulus, Poisson's ratio, and density of neat PA66, nano and micron-sized  $\text{CaCO}_3$  particles are tabulated in Table 1.

## 4. Results and Discussion

### 4.1. Dispersion of Micro- and Nano-particles in the Nylon-66 Matrix

Fig. 1 shows the TEM photomicrograph of the nano-filler used in this study. The average primary particle size the stearic acid coated nano- $\text{CaCO}_3$  filler [9] was measured to be about 33 nm. This image reveals that most of the coated  $\text{CaCO}_3$  nano-particles are quasi-spherical and have rough surface. The nano-particles have a strong tendency to form agglomerates due to their high surface energy which is a result of the small particle size [9].

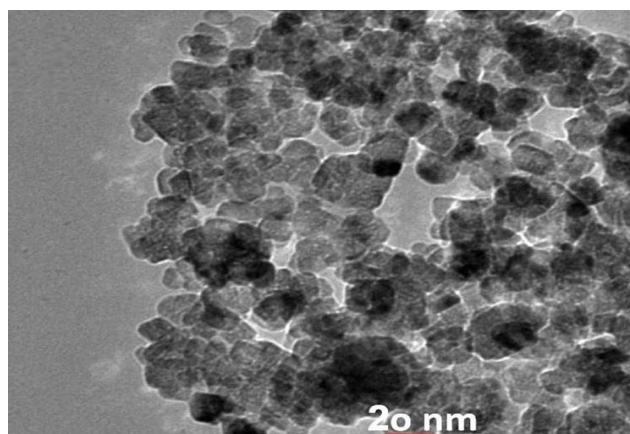


Fig. 1. TEM photomicrograph of the nano- $\text{CaCO}_3$  particles used [in this study] [9]

The dispersion of the particles inside the bulk PA66 was investigated using SEM. It is known that the dispersion of filler in the polymer matrix can have a significant effect on the mechanical properties of the composites. However, the dispersion of inorganic filler in a thermoplastic is not an easy process. The process becomes more intricate when nano-particles are used as filler, because they have strong tendency to agglomerate. It is reported that a good dispersion can be achieved by surface modification of the filler particles [17]. The uniform dispersion of surface modified micro- and nano- $\text{CaCO}_3$  [9] within PA66 is evidenced from SEM images as shown in Figs. 2 & 3. These figures show the different situation of the uniform dispersion of the calcium carbonate micro- and nano-particles in the nylon-66 through various resolutions.

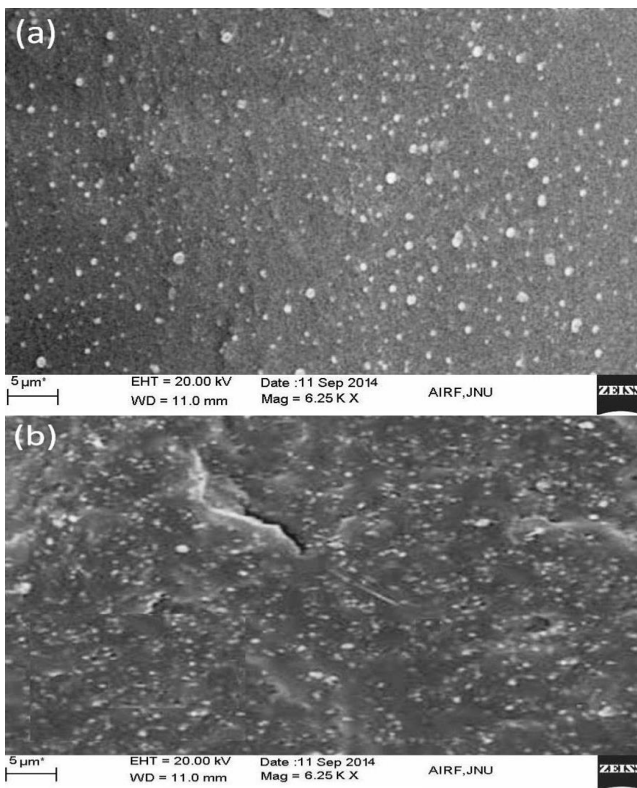
**Table 1.** Young's modulus, Poisson's ratio, and density of neat PA66, micron and nano-sized  $\text{CaCO}_3$ .

Material	Young's modulus (GPa)	density ( $\text{g/cm}^3$ )	Poisson's ratio
Neat PA66 <sup>a</sup>	2.4	1.14	0.42
Micro-sized $\text{CaCO}_3$ <sup>b</sup>	25–50	2.73	0.27
Nanosized $\text{CaCO}_3$ <sup>c</sup>	26	2.93	0.27

<sup>a</sup> Information provided by SRF Lim.

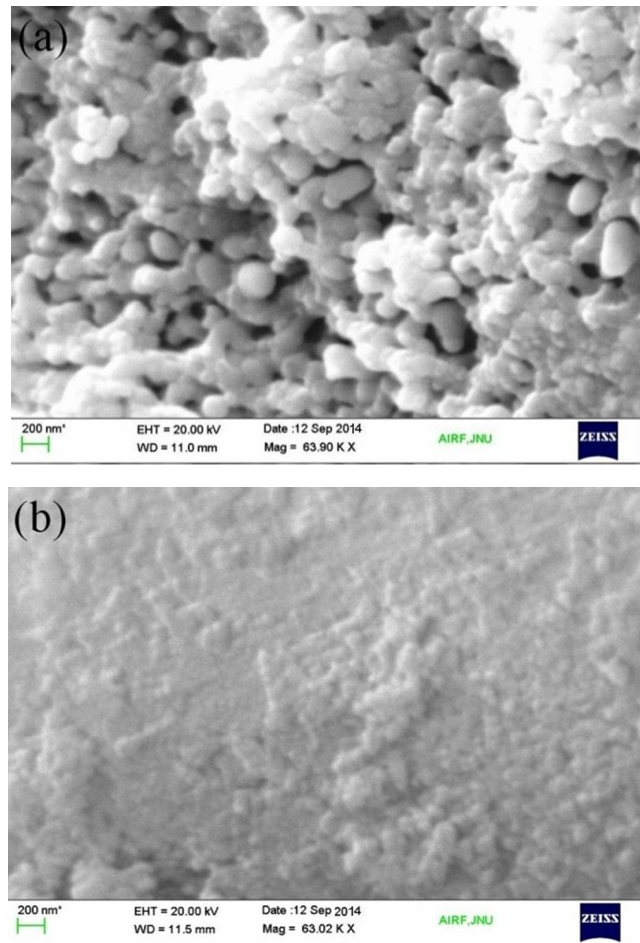
<sup>b</sup> Information provided by Merck Co.

<sup>c</sup> From reference [6].

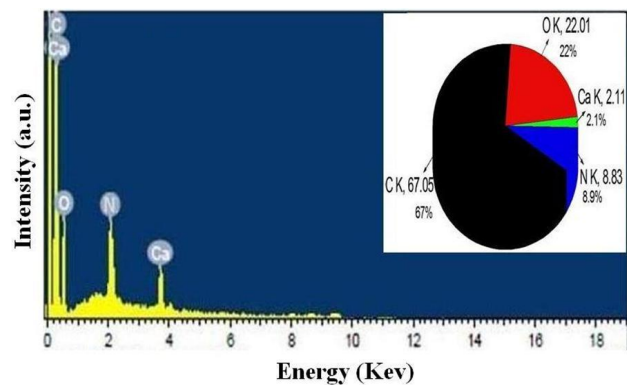


**Fig. 2.** SEM images of PA66/CaCO<sub>3</sub>: a) Micro-composites, b) Nano-composites: magnification of 6.25 kx.

It is clearly noticed from these Figures that both types of surface modified, micro- and nano-particles are covered and quite welded to the PA66 matrix. Moreover, nano-fillers appear homogeneously dispersed into polymer. Referring to Fig. 3(a), it can be seen that some of the cavities, in the nylon-66, are occupied by micro-CaCO<sub>3</sub> particles. However, since no cavity is observed on the surface of PA66/nano-CaCO<sub>3</sub> composites, as noticed in Fig. 3(b), the presence of nano-particles must be more responsible than micro-particles for the cavitations. In the nano-composites containing coated CaCO<sub>3</sub>, the particles are found better welded to the PA66 matrix. In addition, no fracture lines and cavities are present at the interface, suggesting that the coating of CaCO<sub>3</sub> [9] promotes adhesion between the particles and PA66 matrix thus improving the compatibility between the phases. Fig. 4 also shows the presence of CaCO<sub>3</sub> particles in the polymer composites.



**Fig. 3.** SEM images of PA66/CaCO<sub>3</sub>: a) Micro-composites, b) Nano-composites: magnification of 63.90 kx.



**Fig. 4.** Energy-dispersive x-ray (EDS) spectra of PA66/CaCO<sub>3</sub> composites.

#### 4.2. Tensile Properties of Composites

Tensile properties of the seven pieces of each composite sample were examined using Zwick 1445 Universal Testing Machine (UTM). For each piece of all the micro and nano-composite samples, the stress-strain ( $\sigma$ - $\epsilon$ ) data was plotted in terms of elongation. For each sample, 2-3 stress strain ( $\sigma$ - $\epsilon$ ) curves which had significant differences with the others were rejected and the tensile properties calculation was done only based on other ones. The average results were considered as the mechanical property of each sample. The calculated values of the Young's modulus of neat PA66 and PA66/CaCO<sub>3</sub> micro- and nano-composites and the effect of content of micro- and nano-sized CaCO<sub>3</sub> particles on the modulus of PA66/CaCO<sub>3</sub> composites are plotted in Fig. 5. It has been widely accepted that doping of the fillers into polymer matrix would improve the mechanical properties of the synthesized composites [18, 19]. The addition of the CaCO<sub>3</sub> to polymer matrix leads to improvement in stiffness for both the micro-composites and nano-composites. The results shown in Fig. 5 reveal that the Young's modulus of filled polyamide nano-composites is higher than that of micro-CaCO<sub>3</sub>-filled composites.

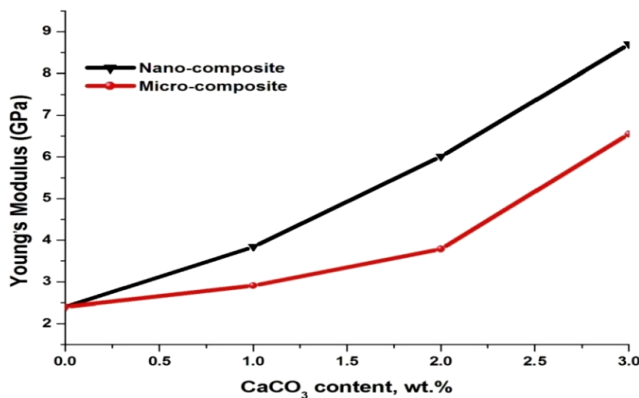


Fig. 5. Effect of filler loading on the Young's modulus of micro- and nano-Polymer composites.

Further, incorporation of CaCO<sub>3</sub> leads to increase in the Young's modulus of polyamide-66 composites in proportion to the filler content. This observation is attributed to the higher reinforcement effect of nano-particles compared to micro particles. Enhancement of the tensile modulus with increasing in filler content can be interpreted as follows. In general, addition of filler to polymer matrix reduces the mobility of polymer chains which causes to more stiffness or higher value of tensile modulus of the polymer composite and also this effect can be raised by increasing the amount of filler. The relationship between weight percentage of filler loading (micro- and nano-CaCO<sub>3</sub>) and strength at yield and break for PA66/CaCO<sub>3</sub> micro- and nano-compos

ites are shown in Figs. 6 and 7.

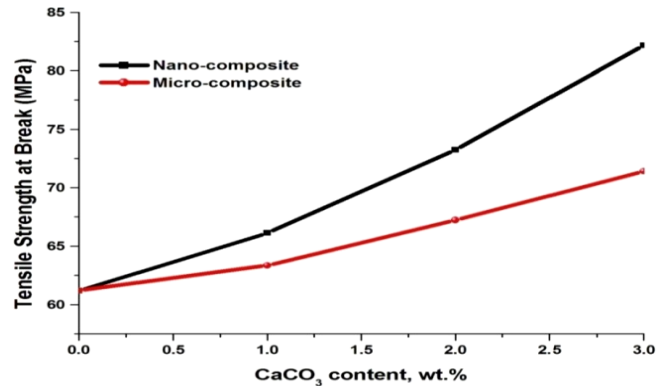


Fig. 6. Variation of tensile strength of micro- and nano-composites with filler loading at break.

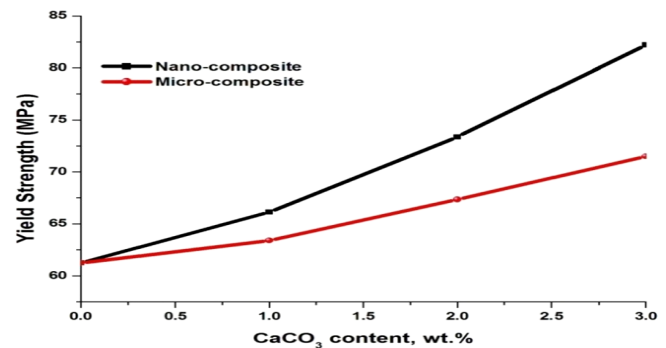


Fig. 7. Variation of tensile strength of micro- and nano-composites with filler loading at yield.

The tensile strength of nano-CaCO<sub>3</sub> filled polyamide composites is recorded higher than that of micro-CaCO<sub>3</sub> filled polyamide composites; the highest loading of the filler (in the range studied) shows the highest tensile strengths of composites and nano-fillers provide higher tensile strength compared to micro-CaCO<sub>3</sub>. This increment in tensile strength is due to uniform dispersion of nano-filler throughout the matrix. The uniform dispersion of nano-CaCO<sub>3</sub> is confirmed by the SEM images shown in Figs. 2 and 3. The reason behind higher tensile strength of nano-composites is the larger surface area of the nano-sized CaCO<sub>3</sub> particles in contact with the polymer matrix. As such, the overall bonding strength between the particles and matrix is higher than neat samples. Thus, it is to be expected that nano-composites could stand higher loading under external forces, as suggested by [20]. When the content of CaCO<sub>3</sub> is low, the micro- and nano-sized CaCO<sub>3</sub> cannot well disperse in the polyamide matrix and agglomerate to form a big cluster and cause a decrease in tensile strength. Elongation percent of composite samples under stress can be calculated from the relation (Equation-13), where  $L_0$  is the initial length of

the test specimen, and  $L$  is the final length of sample after applying the stretching force.

$$\text{Elongation Percent} = \frac{L - L_0}{L_0} \times 100 \quad (13)$$

Figs. 8 and 9 show the dependence of elongation at yield and break points of composites to filler content, respectively.

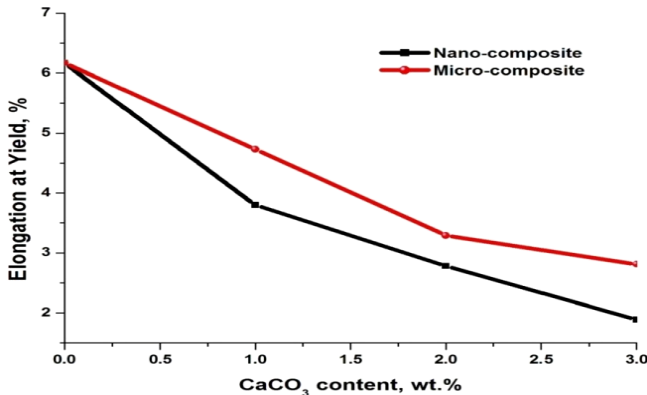


Fig. 8. Variation of elongation of micro- and nano-composites with filler loading at yield.

The incorporation of rigid fillers to polymer matrix reduces the elongation at yield and break. This is a common observation reported by earlier researchers. The results show that with increasing in weight percentage of filler loading, elongation at yield and break for micro- and nano-composites decreases. This might be due to the hard nature of polyamide as well as nano-inorganic filler and also the increment in numbers of spherulites formation with reduction in size and increase in percentage of filler. This may be attributed to the fact that CaCO<sub>3</sub> particles included into the PA66 matrix restrict the movement of polyamide chains. In other words, with the enhancement in rigidity, the ductility of composites decreases; consequently, the composites break at lower elongation as explained by [20].

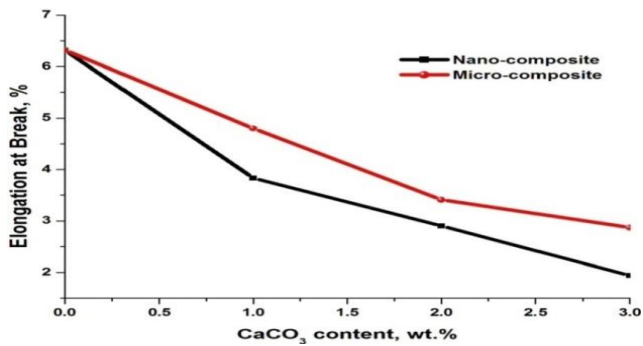


Fig. 9. Variation of elongation of micro and nano-composites with filler loading at break.

### 4.3. Comparison between theoretical and experimental data for Young's modulus

#### 4.3.1. Rule of mixtures

Fig. 10 shows the comparison of predicted Young's modulus from rule of mixtures to experimental data for PA66/CaCO<sub>3</sub> micro- and nano-composites. It is expected that experimental values are within the lower and upper bounds of the rule of mixtures, although this is not observed. This model can be used in two ways: (1) to find an empirical correlation factor for the experimental data and (2) to use this model as a first approximation for predicting the elastic modulus with confidence, as supported by [10].

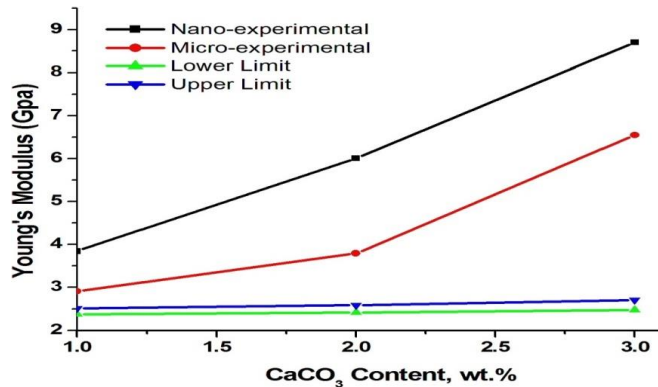


Fig. 10. Comparison of predicted Young's modulus from the mixtures rule to experimental data: micro- and nano-composites.

#### 4.3.2. Guth's Equation and Nicolais-Narkis Theory

These results indicate the limitations of the theories when applied to nano-composites, Figs. 11 and 12. The Guth's equation and Nicolais-Narkis theory are not appropriate model for predicting tensile properties of PA66/CaCO<sub>3</sub> micro- and nano-composites with regard to this fact that the values of experimental results are greater than the calculated values. However, it can be seen that estimated results from this model are similar to those calculated from the mixture rule.

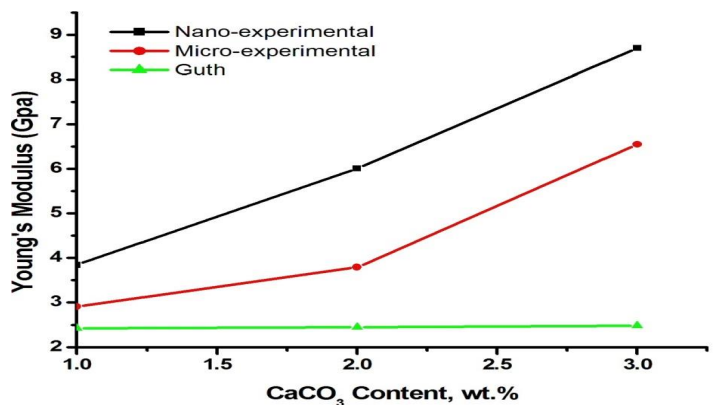


Fig. 11. Comparison of predicted Young's modulus from Guth's equation to experimental data: micro- and nano-composites..



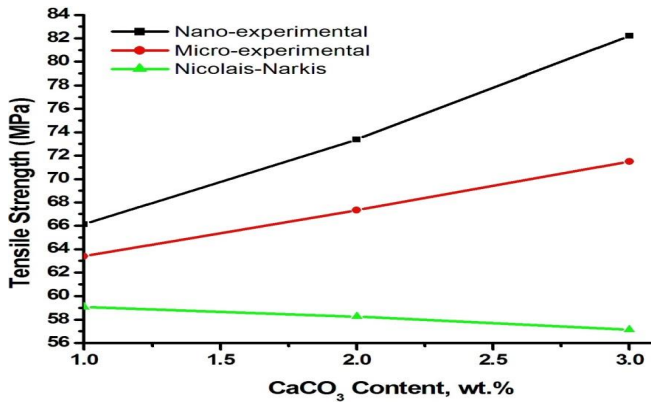


Fig.12. Comparison of predicted yield strength from Nicolais-Narkis theory to experimental data: micro- and nano-composites.

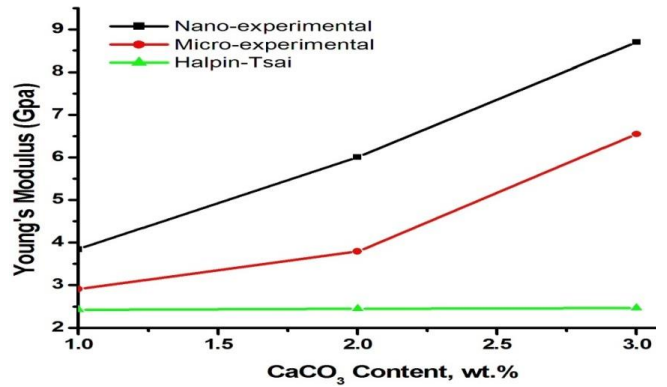


Fig.14. Comparison of predicted Young's modulus from Halpin-Tsai equation with the experimental data.

4.3.3. Hashin-Shtrikman Model

Fig. 13 shows the comparison of predicted Young's modulus from Hashin equations to experimental data for PA66/CaCO<sub>3</sub> micro- and nano-composites. It can be seen that obtained results from this model are substantially similar to those from the rule of mixtures. A similar discussion is applied here.

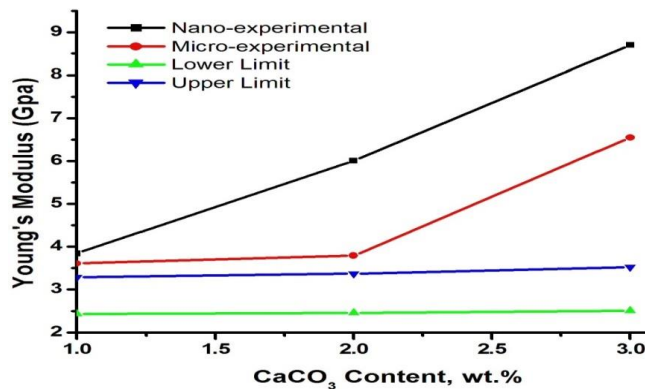


Fig. 13. Comparison of predicted Young's modulus from Hashin-Shtrikman equation to experimental data: micro- and nano-composites.

4.3.4. Halpin-Tsai Model

Comparison of predicted Young's modulus from Halpin-Tsai equations to the experimental data shows that the model is inadequate for predicting the elastic modulus without any correlation, Fig. 14.

It can be concluded from the above discussion that theoretical models developed for particulate composites cannot be applied to predict the elastic modulus of these composites that are very complicated because of the existence of complex interactions between different ingredients in compound. Finally, Fig. 15 shows the results as comparatively.

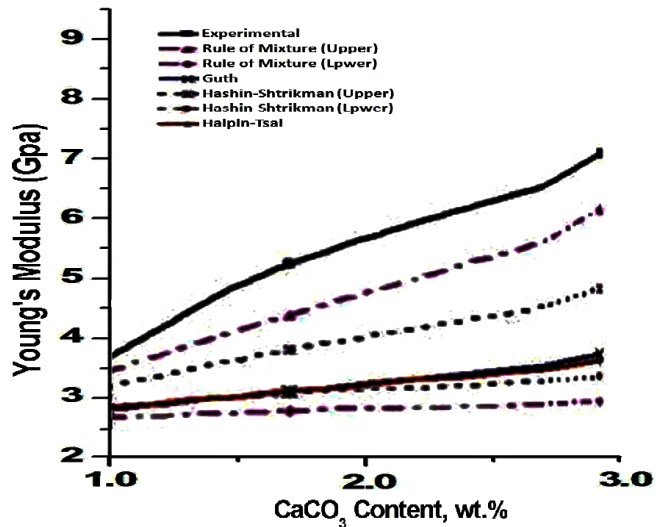


Fig. 15. Comparison of predicted Young's modulus using theoretical and experimental methods.

## 5. Conclusions

From this study, the following conclusions can be drawn:

The calculated values of the Young's modulus of neat PA66 and PA66/CaCO<sub>3</sub> micro- and nano-composites showed that incorporation of CaCO<sub>3</sub> leads to increase in the Young's modulus of nylon-66 composites in proportion to the increase content of the filler and this observation is attributed to the higher reinforcing effect of nano-particles compared to micro particles. It was also observed that the tensile strength of nano-CaCO<sub>3</sub> filled polyamide composites is higher than that of micro-CaCO<sub>3</sub> filled polyamide composites; the highest loading of the filler (in the range studied) shows the highest tensile strengths of composites and nano-fillers provide higher tensile strength compared to micro-CaCO<sub>3</sub>. The results showed that with increasing in weight percentage of filler loading, elongation at yield and break for micro and nano-composites decreases. It is well known that one of the most important aspects of material development in thermoplastics engineering is to achieve a good combination of mechanical properties and process ability at a moderate cost. The obtained results, in this study, demonstrated that adding filler to polymer matrix reduces the mobility of polymer chains which in effect causes more stiffness or higher value of tensile modulus of the polymer composite. It is strongly dependent on shape, size, aggregate size and degree dispersion of filler in the polymer matrix which can have a significant effect on the mechanical properties of the composites, and it may be achieved by surface modification of the filler particles. The uniform dispersion of surface modified micro- and nano-CaCO<sub>3</sub> within PA66 was evidenced from SEM images. It has been demonstrated through this study that the properties of the composites are significantly superior to the virgin polyamide. The estimated mechanical properties using different theoretical models available in literature were compared with the experimental data for Young's modulus and yield stress. It was found that the predicted values from the theoretical models were lower than the observed properties. Thus, it may be concluded that models developed for particular composites cannot be applied to predict the elastic modulus of the micro- and nano-composites synthesized in the present study under different set of conditions. Nevertheless, the theoretical models may be used with some degree of confidence to predict the elastic modulus as an initial estimation or first approximation.

## Acknowledgment

This scientific product was extracted through a research project implemented from funding of research projects of Yasouj Branch, Islamic Azad University.

## References

- [1] L. Jiang, Y. C. Lam, K. C. Tam, T. H. Chua, G.W. Sim, L. S. Ang, Strengthening acrylonitrile-butadiene-styrene (ABS) with nano-sized and micron-sized calcium carbonate, *Polymer*, 46 (2005) 243–252.
- [2] K. Magniez, E. Bafekrpour, B. L. Fox, M. G. Looney, Structure–Property Relationships in Nylon 6 Nano-composites Based on Octaphenyl-Dodecaphenyl–POSS, Montmorillonite, and Their Combinations, *Polym. Compos.* 36 (2015) 153–160.
- [3] L. Gonzalez, P. Lafleur, T. Lozano, A. B. Morales, R. Garcia, Mechanical and thermal properties of polypropylene/montmorillonite nanocomposites using stearic acid as both an interface and a clay surface modifier, *Polym. Compos.* 35 (2014) 1–9.
- [4] D. S. Maleki, M. J. Barzegar, M. H. Zarrintan, K. H. Adibkia, F. Lotfipour, Calcium carbonate nanoparticles: Potential in bone and tooth disorders, *J. Pharm. Sci.* 20 (2015) 175–182.
- [5] X. Wang, D. Wu, Y. Song, R. Jin, Nano-composites of poly(vinyl chloride) and nano-metric calcium carbonate particles: Effects of chlorinated polyethylene on mechanical properties, morphology and rheology, *J. Appl. Polymer Sci.* 92 (2004) 2714–2723.
- [6] C. M. Chen, Y. K. Cheung, PP/CaCO<sub>3</sub> Nano-composites, *Polymer* 43 (2002) 2981–2992.
- [7] X. Jia, M. Herrera-Alonso, T. J. Mc-Carthy, Surface modification; Part 1: Targeting the amide groups for selective introduction of reactive functionalities, *Polymer* 47 (2006) 4916–4924.
- [8] J. Jordan, I. J. Karl, R. Tannenbaum, M. A. Sharaf, I. Jasiuk, Experimental trends in polymer nanocomposites: A review, *Mater. Sci. Eng. A*, 393 (2005) 1–11.
- [9] A. J. G. Ghadami, M. Idrees, Characterization of CaCO<sub>3</sub> nanoparticles synthesized by reverse micro-emulsion technique in different concentrations of surfactants, *Iran. J. Chem. Chem. Eng.*, 32 (2013) 27–35.
- [10] M. Haghighat, A. Zadhoush, S. Nouri Khorasani, Physicomechanical properties of  $\alpha$ -cellulose-filled styrene–butadiene rubber composites, *J.*

- Appl. Polymer Sci. 96 (2005) 2203–2211.
- [11] Q. X. Zhang, Z. Z. Yu, X. L. Xie, Y. W. Mai, Crystallization and impact energy of polypropylene/CaCO<sub>3</sub> nano-composites with nonionic modifier, *Polymer* 45 (2004) 5985–5994.
- [12] R. Wang, Pyrz, Prediction of the overall moduli of layered silicate-reinforced nano-composites-Part II: Analyses, *Compos. Sci. Technol.* 64 (2004) 935–944.
- [13] V. A. Buryachenko, A. Roy, K. Lafdi, K. L. Anderson, S. Chellapilla, Multi-scale mechanics of nano-composites including interface: Experimental and numerical investigation, *Compos Sci Technol.*, 65 (2005) 2435–2465.
- [14] X. L. Xie, Q. X. Liu, R. K. Y. Li, X. P. Zhou, Q. X. Zhang, Z. Z. Yu, Y. W. Mai, Rheological and mechanical properties of PVC/CaCO<sub>3</sub> nano-composites prepared by in situ polymerization, *Polymer* 45 (2004) 6665–6673.
- [15] E. D. Bliznakov, C. C. White, M. T. Shaw, Mechanical properties of blends of HDPE and recycled urea-formaldehyde resin, *J. Appl. Polymer Sci.* 77 (2000) 3220–3227.
- [16] R. Brendan, Thin film testing - ASTM D882, in *Annual Book of ASTM Standards*. ASTM International Publisher, Philadelphia, 1 (2002) 160–168.
- [17] M. Chen, Y. Feng, L. Wang, L. Zhang, J. Zhang, Study of palladium nano-particles prepared from water-in-oil micro-emulsion. *Collo. Surf. A: Physicoch. Eng. Aspec*, 281 (2006) 119–124.
- [18] J. Cayer-Barrioz, D. Ferry, K. Frihi, R. Cavalier, G. V. Seguela, Microstructure and mechanical behavior of polyamide 66-precipitated calcium carbonate composites: Influence of the particle surface treatment, *J. Appl. Polymer Sci.* 100 (2006) 989–999.
- [19] H. Hanim, R. Zarina, M. Y. F. Ahmad, Z. A. Mohd, A. Hassan, The effect of calcium carbonate nanofiller on the mechanical properties and crystallisation behaviour of polypropylene, *Malays. Polymer J.* 3 (2008) 38–49.
- [20] B. K. Zhu, S. H. Xie, Z. K. Xu, Y. Y. Xu, Preparation and properties of the polyimide/multi-walled carbon nano-tubes (MWNTs), *Compos. Sci. Technol.* 66 (2006) 548–554.