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The influence of size and content of Libyan limestone particles on the mechanical properties of high-density of polyethylene

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Nano-composite material
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A B S T R A C T

This study investigated the effect of size and content of Libyan limestone (calcium carbonate ($CaCO_3$)) particles on mechanical properties of high-density polyethylene (HDPE). CaCO3 rocks were crushed and ground into nano and coarse sizes using a hammer mill and a centrifugation ball mill. HDPR/$CaCO_3$ Composites containing 10, 20 and 30% $CaCO_3$ prepared using polyethylene glycol (PEG) as a coupling agent. The mechanical properties including; impact strength, tensile strength, young's modulus and Shore hardness was evaluated. The correlation between mechanical properties and the amount and size of $CaCO_3$ was also investigated. X-ray diffraction (XPD) results illustrated that the average sizes of the coarse and fine $CaCO_3$ particles were 74 nm and 1 nm, respectively. The results that the impact strength was decreased significantly with the addition and increasing the amount of $CaCO_3$. On the other hand, the tensile strength was increased with increasing the content of $CaCO_3$ up to 20%, and then decreased. Young's modulus and Shore hardness were increased with the increasing the $CaCO_3$ content. As expected, fine (nano) $CaCO_3$ composites demonstrated better overall mechanical properties than composites made with coarse $CaCO_3$. The results showed also a strong positive relationship between size and content of $CaCO_3$ with most of the studied mechanical properties. Most importantly, Libyan $CaCO_3$ showed to be an excellent reinforcing material for polyethylene since it enhanced its mechanical properties and has the potential to reduce the production cost of these materials.

تأثير حجم وكمية جسيمات الحجر الجيري الليبي على الخواص الميكانيكية للبولي إيثيلين عالي الكثافة

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الملخص

هدفت هذه الدراسة إلى دراسة تأثير حجم وكمية جسيمات الحجر الجيري الليبي (كربونات الكالسيوم ($CaCO_3$)) على الخواص الميكانيكية للبولي إيثيلين عالي الكثافة (HDPE). تم سحق صخور $CaCO_3$ وطحنها إلى أحجام نانوية وخشنة باستخدام مطحنة مطرقة ومطحنة كرات الطرد المركزي. تم تحضير مركبات $CaCO_3$/HDPE بنسب 10 و20 و30 % من $CaCO_3$ بنوعيه الناعم والخشن باستخدام بولي إيثيلين جلايكول (PEG) كمادة رابطة. بعد ذلك تم تقييم الخواص الميكانيكية مثل مقاومة الصدمة، قوة الشد، ومعامل يونغ وصلادة شور. كما تم التحقيق من علاقة الارتباط بين الخصائص الميكانيكية وكمية وحجم $CaCO_3$. أظهرت نتائج حيود الأشعة السينية (XRD) أن

الكلمات المفتاحية:

كربونات الكالسيوم الليبية
الخصائص الميكانيكية
حجم ومحتوى جسيمات كربونات الكالسيوم
بولي أيثيلين

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متوسط أحجام جسيمات $CaCO_3$ الخشنة والناعمة كانت 74 نانومتر و1 نانومتر على التوالي. اظهرت النتائج حدوث انخفاض ملحوظ في خاصية مقاومة الصدم بعد إضافة $CaCO_3$ وزيادة محتواها. وبالعكس تماماً، أشارت النتائج إلى أن قوة الشد ازدادت بزيادة محتوى $CaCO_3$ حتى نسبة 20%، كما ازداد معامل يونغ وصلادة شور بزيادة محتوى $CaCO_3$. كما هو متوقع، أظهرت مركبات $CaCO_3$ الناعمة (النانوية) خصائص ميكانيكية أفضل من المركبات المصنوعة من $CaCO_3$ الخشنة. كما أظهرت النتائج وجود علاقة إيجابية قوية بين الحجم ومحتوى $CaCO_3$ ومعظم الخصائص الميكانيكية. وبهذا أثبت الحجر الجيري الليبي أنه مادة تقوية ممتازة للبولي إيثيلين، من خلال تحسينه لخواصه الميكانيكية، وقدرته على خفض تكلفة الانتاج لهذه المواد.

1. Introduction

The global plastics market is growing rapidly, with 380 million tons produced in 2020 and expected to reach over 1.1 billion tons by 2050 [1-2]. The most widely produced plastic is polyethylene (PE). Applications for PE are numerous and include medical replacement implants, tubing, and packaging films. The three primary forms of polyethylene are linear low-density polyethylene (LLDPE), low-density polyethylene (LDPE), and high-density polyethylene (HDPE). PE is a thermoplastic material with low cost, excellent processability, good electrical insulation, toughness, flexibility, and chemical stability. It has low barrier properties to gases, aromas, and fats. As density increases, barrier properties increase, while impact resistance, toughness, and transparency decrease [3-5]. On the other hand, PE is non-biodegradable polymer with poor mechanical properties, as seen by its low tensile strength, and weak creep resistance [6]. In order to address these shortcomings and produce material with better qualities, fillers are added to the PE matrix. In general, fillers are used to increase the bulk polymer, lower costs, and enhance the polymer's properties. In fact, PE has been reinforced with a variety of fillers, both organic and inorganic.

Calcium carbonate ($CaCO_3$) is a filler that is commonly used to enhance the properties of PE composites due to its low cost and availability. One of the most prevalent substances in the earth's crust is CaCO3, which creates rocks like chalk and limestone [7]. According to Adeosun et al. [8] $CaCO_3$ is an inexpensive, non-toxic, inorganic material that is frequently employed as a filler in polymer composites to enhance their properties. Wang et al. [9] found that the tensile and flexural modulus of PE composite evidently increased by the addition of $CaCO_3$ as compared to pure polymers. Sahebian et al. [10] stated that the presence of $CaCO_3$ nanoparticles in the polymer matrix improves the mechanical and thermal stability of the polymer. Shi et al. [11] found that the tensile yield strength of HDPE was increased after the addition of $CaCO_3$. Additionally, they revealed that cubic $CaCO_3$ might have a detrimental influence on toughness and that sphere-shaped $CaCO_3$ is the ideal form for enhancing thermal stability. Zapata et al. [12] revealed that PE/$CaCO_3$ nanocomposites provide a way to enhance the low degradation of LDPE without compromising the polymer properties, which will enable the production of new environmentally friendly polymers in the future. They suggest that these nanocomposites may be used in agriculture as films. Practically, the addition of compatibilizers or the treatment of $CaCO_3$ are known to enhance the performance and properties of PE/ $CaCO_3$ composites.

It is important to emphasis that $CaCO_3$ is a polar filler, hence it isn't compatible well with non-polar matrices like PE. This may cause the $CaCO_3$ particles to aggregate, which subsequently leads to poor compatibility (weak adhesion at the interface between CaCO3and PE matrix) [13]. These are the main reasons why the mechanical properties of polymer composites can be significantly declined after the addition after the addition of $CaCO_3$. According to Cao et al. [14] stearic acid treatment of $CaCO_3$ by stearic acid resulted in a slight increase in yield strength of HDPE/ $CaCO_3$. Others [15] found that stearic acid surface treatment of $CaCO_3$ could result in better dispersion and fewer aggregates, increasing the material's tensile strength. Cao et al. [14] declared that stearic acid is a common and affordable materials that is used to enhance the hydrophobic properties of $CaCO_3$ and improve the mechanical, thermal, and physical behavior of their composites. Demjén et al. [16] observed that silane-treated $CaCO_3$ significantly increased the polypropylene (PP)/$CaCO_3$ composites' tensile strength in comparison to untreated ones. Furthermore, study by Atikler et al. [17] revealed that silane treatment significantly enhanced the mechanical characteristics of the HDPE composites filled with fly ash and $CaCO_3$.

On the other hand, it is found [18] that the use of compatibilizers such as malic anhydride grafted polypropylene (PP-g-MA) considerably enhances the strength properties and improves $CaCO_3$ dispersion and interfacial adhesion in PP/$CaCO_3$ composite. Also, anhydride grafting high HDPE (HDPE-g-MA) was used successfully as a compatibilizers in composites based on HDPE and polylactide to improve their properties and performance. Additionally, anhydride grafted HDPE (HDPE-g-MA) has been effectively employed as a compatibilizer to enhance the performance and properties of composites made of HDPE and polylactide [19]. Other types of compatibilizers such as ethylene-octene copolymer grafted with MA (POE-g-MA), and ethylene-vinyl acetate copolymer grafted with MA (EVA-g-MA) were applied effectively to improve the dispersion of $CaCO_3$ into PP matrix, resulting in an increase in the tensile strength and modulus [20]. The main aim of this study is to investigate the influence of size and content of Libyan $CaCO_3$ on the mechanical properties of HDPE/$CaCO_3$ composites. In this investigation, polyethylene glycol (PEG) would be employed as a compatibilizer. PEG is a synthetic, multipurpose, and highly hydrophilic polymer with a variety of functional end groups and chain lengths [21]. It is a polymer that can be used in a wide range of applications due to its overwhelming properties. With exception to HDPE/$CaCO_3$ composites, PEG has been successfully employed as a compatibilizer in various polymer composite systems [22-24].

In summary, the utilization of Libyan $CaCO_3$ in the field of polymer composite has received little attention, despite the fact that it is a worthwhile area for research and development. Therefore, research in this area should get priority, particularly because it is predicated on utilizing one of the most significant and readily available local resources. It should be emphasis that $CaCO_3$ are widespread over large area through Libya [25]. The main benefits of using $CaCO_3$ as a filler in polymer composites are cost reduction, enhanced properties. And sustainability [26]. For example, $CaCO_3$ is abundant and locally available in many regions, reducing dependency on expensive filler. Moreover, it can enhance the mechanical, physical properties and thermal properties of the host polymer. It can also work as white pigment to improve the whiteness and brightness. Likewise, $CaCO_3$ can lower environmental footprint by reduce overall polymer consumption by partially replacement with mineral filler. Finally, $CaCO_3$-filled polymer can be recycled effectively [27].

2.Experimental Work

2.1Material

HDPE (SABIC FE00952) was used as a matrix. HDPE specifications are presented in table 1. $CaCO_3$ was collected from Tarhuna city as a rock. After being ground, $CaCO_3$ was used as a filler. PEG (Northampton company in UK) with an average molecular weight of 5500-6500 was used as a coupling agent. P-xylene (Alfa Aesar (99%)) was used to ensure good mixing and homogeneity of the composites.

Table 1: The specification of HDPE.

Property type	Property value
Density/g.cm^3	0.952 (ISO 1183)
Melt flow index g/min	0.05 at 190°C and 2.16 kg /(ISO1133)

2.2 Preparation of $CaCO_3$

The limeston rocks were smashed manually to reduce the size into small piesess. Then the small piesess placed in a hammer machine (hammer muehle HW1-2008, Germany) to attain $CaCO_3$ in form of powder. After that, a portion of $CaCO_3$ was placed in ball milling machine (Model S100, Retsch GmbH) to gain fine $CaCO_3$ podwer. The machine was set on a speed of 500 RPM at 60 min with an interval of 0.05 h. The grinding ratio was 1:10 (100 G to 1kg). In order to create a sufficient amount of fine $CaCO_3$. this procedure was repeated several times.

2.3 Composites preparation method

HDPE, $CaCO_3$ and PEG were mixed by adding small amount of xylene in order to produce a liquefied mixture with high level of homogeneity. After that, the mixture was poured in a beaker and heated at 105 °C with continuous hand stirring using a stirring glass rod to prevent any agglomeration. The mixture was then placed into a rolling machine to obtain sheets. Afterward, the sheets were dried from xylene by oven drying (Witeg machine) at a temperature of 80 °C for about 24 h. The sheets are then cut into small sizes in order to be placed them in mini-extruder (HAAK Mini; CTW-Twin-screw), which is set on a temperature of 150° C and the spinning speed of 50 rpm. Composites with different $CaCO_3$ sizes and content were prepared. The compositions of each composite prepared in this study is displayed in Table 2.

Table 2. Compositions of each composite prepared in this study

No	HDPE, wt. %	Coarse $CaCO_3$, wt. %	Fine $CaCO_3$, wt. %	PEG, wt. %
1	100	0	0	0
2	88	10	0	2
3	78	20	0	2
4	68	30	0	2
5	88	0	10	2
6	78	0	20	2
7	68	0	30	2

The injection moulding machine (Xplore12ml) was used to prepare the specimens for mechanical properties tests. The machine was set on a temperature of 160 °C, a pressure of 16 bar and the mold temperature at 50°C.

3.Characterization

3.1X-ray Diffraction

X-ray diffraction (XRD) (PW 1800 X-ray Diffraction) were used in this study to determine the phase composition and $CaCO_3$ particle size for both coarse and fine particles. Data were collected over a 2-theta in the range of 20–80 with a time step of 2.90 s The crystallize size was calculated from XRD data by Scherrer equation.

3.Mechanical properties tests

- **Impact strength test**

The Charpy impact test was performed in this study to measure the impact strength resistance using (CEAST Resil Impactor tester) at room temperature with impact energy of 15 J. The specimens for impact strength test were prepared by making a V-shape notch according to ASTM (D256-10). A minimum of five specimens was tested for each composite.

- **Tensile strength test**

Tensile strength test was accomplished according to ASTM D638. This test was performed by applying a tensile force to a sample specimen and measuring various properties (tensile strength and young's modulus) of the specimen under stress. It is conducted on a universal testing machine (Zwick roell ProLinefor), at speed test of 250 mm/min and the grip-to-grip separation at the start position of 0.0388 mm. A minimum of three specimens was tested for each composite.

- **Hardness test**

The Shore hardness tests were performed according to standard method (D2240 /ISO 868), and type D type using (Ray-Ran Machine, Model RR/B550, UK made). About ten easements were taken for each composite.

4.Results and Discussion

4.1XRD results

The XRD patterns observed of coarse and fine $CaCO_3$ particles are shown in Figures 1 and 2. The distinctive peaks in the XRD patterns represent the stable phase of calcite. According to obtained data, the purity of $CaCO_3$ was 100%. Most significantly, it was found that the average crystallite sizes of the coarse and fine $CaCO_3$ particles were 1 mm and 74 nm, respectively.

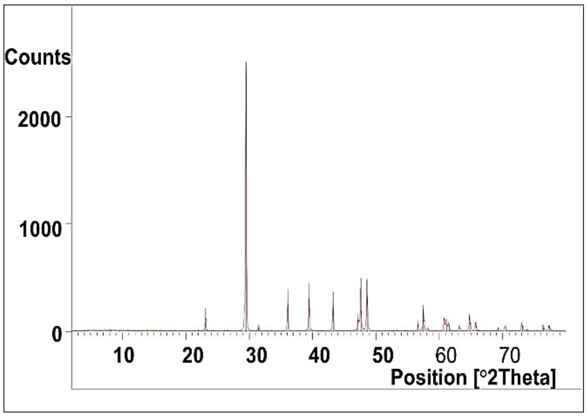

Figure 1: XRD patterns of coarse $CaCO_3$ particles.

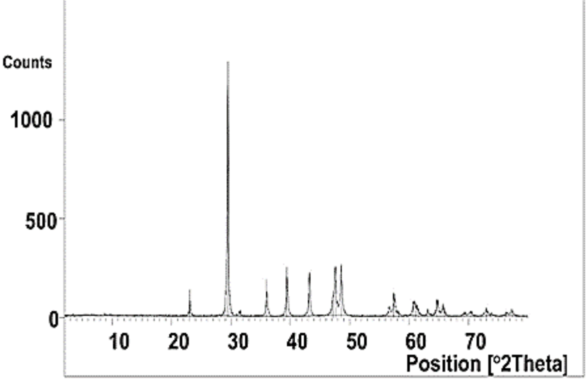

Figure 2: XRD patterns of fine $CaCO_3$ particles.

4.2.Impact strength results

As shown in Figure 3, the impact strength was decreased with the addition of both types of $CaCO_3$. The impact strength value of pure HDPE (192.5 KJ/m^2) was higher than those of all the HDPE/ $CaCO_3$ composites. In the case of composites of fine $CaCO_3$, the impact strength was decreased with increasing the fine $CaCO_3$ content. It decreased from 192.5 KJ/m^2 (for HDPE) to 6.64 KJ/m^2 (for composites with 30% $CaCO_3$). Whereas, in the case of composites with coarse $CaCO_3$, the impact strength decreased after the addition of 10% $CaCO_3$ (34.23 KJ/m^2) and increased (53.56 KJ/m^2) when 20% $CaCO_3$ content was added. Adding 30% coarse $CaCO_3$ decreased the impact strength (8.64 KJ/m^2) again. Most importantly, the impact values of composites with coarse $CaCO_3$ were higher than that of composites with fine $CaCO_3$.This means that coarse size more effective at absorbing and dissipating impact energy than fine size of $CaCO_3$. The decrease in the impact strength after adding the $CaCO_3$ to HDPE was mentioned by many authors [28-29]. The decreases in the impact strength is due to the reduction of elasticity, deformability of matrix and its ability to absorb deformation energy [31].

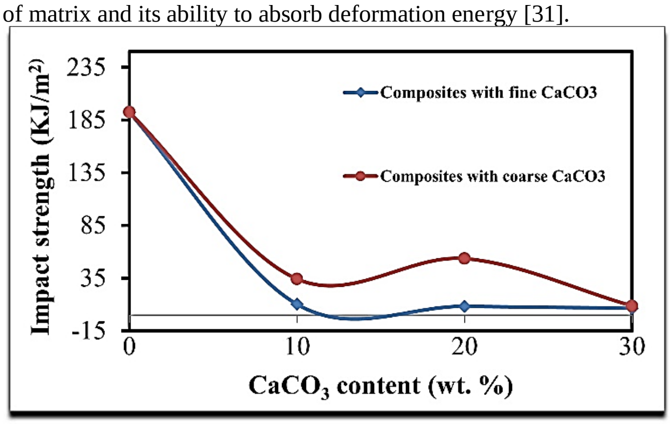

Figure 3: Effect of size and content of $CaCO_3$ on impact strength.

4.1.1. Correlation of content and size of $CaCO_3$ and impact strength

As shown in Figures 4 and 5, the impact strength of HDPE composites with both sizes of $CaCO_3$ were highly correlated with the $CaCO_3$ content. These results indicate strong positive relationships, which means a strong positive correlation between $CaCO_3$ content and impact property. The coefficient of determination in the case of composites with fine $CaCO_3$ content and impact strength was ($R^2 = 0.6167$); indicating a strong correlation and very strong positive relationship. In the same vein, the coefficient of determination in the case of composites with coarse $CaCO_3$ content and impact strength was ($R^2 = 0.7052$): indicating a strong correlation and very strong positive relationship.

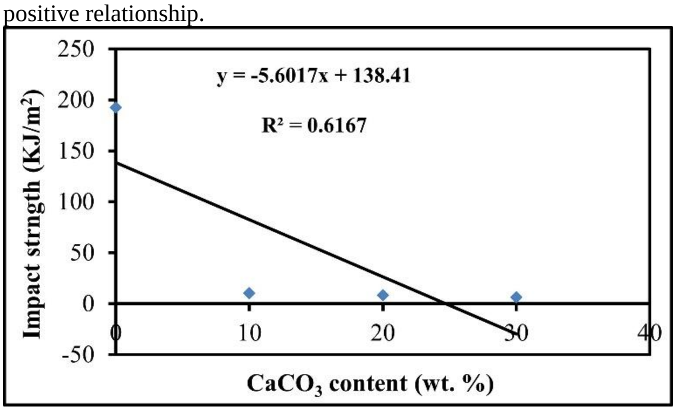

Figure 4: Correlation of size and content of fine size of $CaCO_3$ on impact strength.

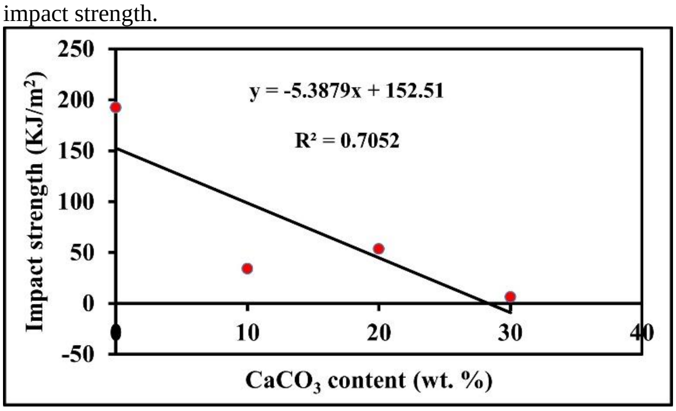

Figure 5: Correlation of size and content of coarse of $CaCO_3$ with impact strength.

4.2. Tensile strength results

Figure 6 illustrated the effect of adding of both coarse and fine $CaCO_3$ particles on the tensile strength of HDPE/ $CaCO_3$ composite. There is a slight an improvement in the tensile strength in both cases. With exception to tensile value of composites with 30% coarse $CaCO_3$ (12.89 MPa), all composites (14.18-15.47 MPa) showed higher strength than pure HDPE (13.19 MPa).

The decrease in tensile strength at 30% of coarse $CaCO_3$ might be due to the formation of agglomeration, which results in weak adhesion between the matrix and coarse filler [32]. In fact, at high loading, filler tends to form clusters. Theses act like defects of voids, reducing the strength instead of reinforcing the composites. So, these defects of voids could adversely affect the mechanical properties of polymers. Moreover, tensile strength mainly comes from the polymer chain's ability to stretch and carry load. Subsequently, higher filler content reduces the continuity of the polymer phase, lowering strength.

The tensile strength was relatively higher in the case of fine $CaCO_3$ than in the coarse case. This indicates that fine $CaCO_3$ particles (with nano-sized scale) appears to produce composites with higher tensile strength properties in comparison to higher particle $CaCO_3$ size (with micro-sized scale). The highest tensile strength (15.47 MPa) was obtained by composites with 30% fine $CaCO_3$ content. This was expected because particle size has an obvious effect on these mechanical properties. It is well known that smaller $CaCO_3$ particles provide higher strength of filled polymers [34].

These results were in agreement with many published studies [32-33]. The tensile strength and ductility of the polymers found to decrease as the percentage of $CaCO_3$ increases in the range of 5 to 20% [33]. Awan et al. [33] showed that the addition of $CaCO_3$ in the range of 5 to 10% shows a significant improvement in mechanical properties including in the tensile strength. On the other hand, research by Ngothai et al. [32] declared that the tensile strength of the mixture of HDPE and rHDPE is slightly affected by the particle size of $CaCO_3$, where the smaller the size, the greater the tensile strength. It well known that the impact of $CaCO_3$ particles was attributed to their large interfacial surface and small particle size, which create a strong adhesion between the polymer matrix and the filler [35].

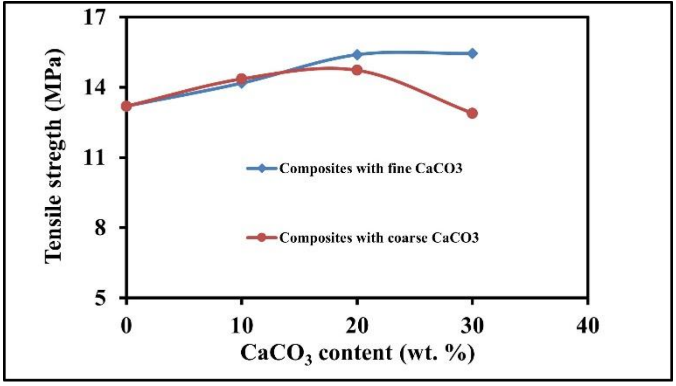

Figure 6: Effect of Size and Content of $CaCO_3$ on tensile strength.

4.2.1. Correlation of content and size of $CaCO_3$ on tensile strength

As shown in Figure 7, the tensile strength of HDPE composites with fine $CaCO_3$ was highly correlated with the $CaCO_3$ content. These results indicate very strong positive relationships, which means a strong positive correlation between $CaCO_3$ size and content and tensile strength property. The coefficient of determination in the case of composites with fine $CaCO_3$ content and tensile strength was ($R^2 = 0.9094$): indicating a very strong correlation and very strong positive relationship.

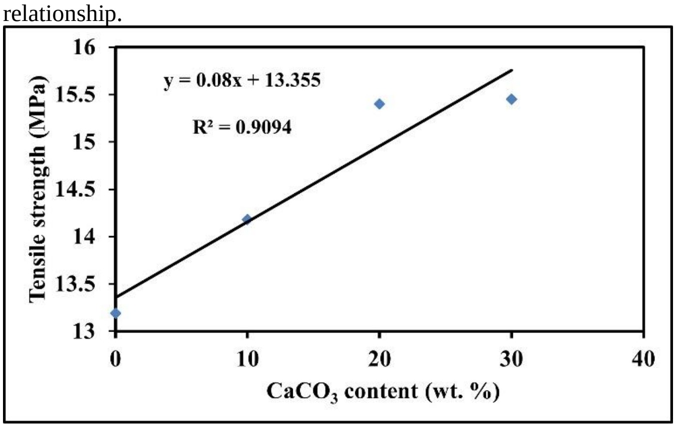

Figure 7: Correlation of size and content of fine $CaCO_3$ on tensile strength.

Conversely, the tensile strength of HDPE composites with coarse $CaCO_3$ was not correlated with the size and content of $CaCO_3$. As shown in Figure 8, the coefficient of composites with coarse $CaCO_3$ content and tensile strength was ($R^2 = 0.4856$): indicating no relationship between them.

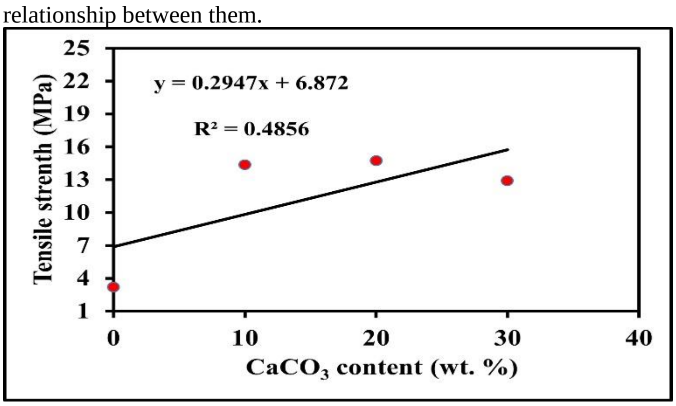

Figure 8: Correlation of size and content of coarse $CaCO_3$ on tensile strength.

4.3. Young’s modulus results

As demonstrated in Figure 9, the young’s modulus was increased with the increasing the $CaCO_3$ content into HDPE matrix in both cases (fine and coarse $CaCO_3$).

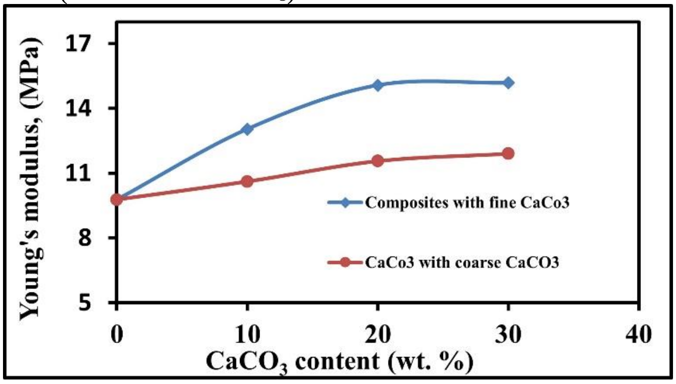

Figure 9: Effect of size and content of $CaCO_3$ on Young’s modulus.

The young’s modulus was initially 9.77 MPa for HDPE. After the addition of fine $CaCO_3$, young’s modulus increased to 13.04, 15.07, and 15.18 MPa, as the amount of $CaCO_3$ increased from 10 to 20 to and 30%, respectively. In the case of coarse $CaCO_3$, there was a very slight increase in young’s modulus. The young’s modulus increased to 10.61 MPa with the addition of 10% $CaCO_3$, to 11.56 MPa with the addition of 20% $CaCO_3$, and then to 11.90 with the addition of 30% $CaCO_3$. The effect of particle size of $CaCO_3$ on the young’s modulus was more pronounced in the case of fine particles compared to the coarse ones. The results were consistent with several studies [36-37]. In general, smaller particle size results in greater improvement of modulus [38] Increase in properties such as modulus suggest decrease in polymer chain mobility brought about by the presence of the stiff particles between the polymer macromolecules, restraining their movement in the solid state [39].

4.3.1. Correlation of content and size of $CaCO_3$ Young’s modulus

As illustrated in Figures 10 and 11, the young’s modulus results showed an increase with increasing both fine and coarse $CaCO_3$. These findings reveal a robust positive relationship, signifying a strong positive correlation between $CaCO_3$ size and content on young’s modulus. The coefficient of determination (R^2) for composites with fine $CaCO_3$ and young’s modulus was 0.8687, indicating a strong correlation and a highly significant positive relationship. Similarly, for composites with coarse $CaCO_3$, the coefficient of determination (R^2) was 0.9682, confirming a strong correlation and an exceptionally strong positive relationship. These results underscore the significant influence of $CaCO_3$ content on the young’s modulus of the composites.

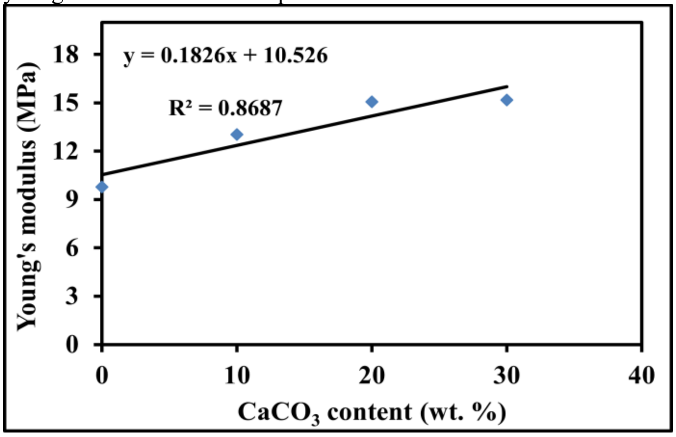

Figure 10: Correlation of size and content of fine $CaCO_3$ with Young’s modulus.

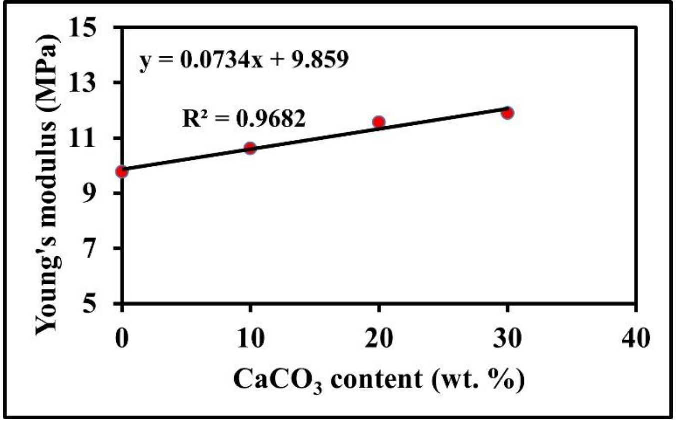

Figure 11: Correlation of size and content of coarse $CaCO_3$ with Young’s modulus.

4.4. Shore hardness

The effect of content and size of $CaCO_3$ on hardness properties of HDPE/$CaCO_3$ composites is shown in Figure 12. In the case of fine $CaCO_3$, the hardness was increased with increasing the amount $CaCO_3$. The hardness was increased from 48 (for HDPE) to 54 (for composite with 30% fine $CaCO_3$. On the other hand, the hardness was increased with increasing the amount of coarse $CaCO_3$ up to 20%, and then negligibly decreased when 30% of coarse $CaCO_3$ was added. In all cases the values of hardness were higher than that of pure HDPE. It is clear that the fine $CaCO_3$ had relatively better impact on hardness properties than coarse one. These results are in agreement with many published studies [40-41].

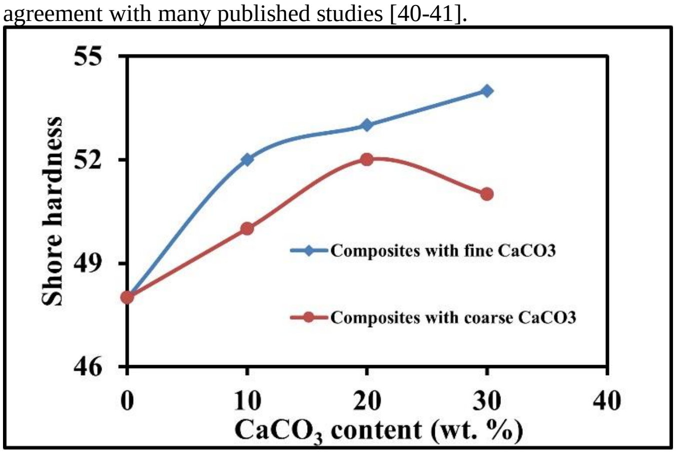

Figure 12: Effect of size and content of $CaCO_3$ on hardness.

4.3.1. Correlation of content and size of $CaCO_3$ Young’s modulus

As shown in Figures 13 and 14, the shore hardness results of HDPE composites with both sizes of CaCO3 were highly correlated with the $CaCO_3$ size and content. These results indicate very strong positive relationships, which means a strong positive correlation between $CaCO_3$ content and this property. The coefficient of determination in the case of composites with fine $CaCO_3$ content and shore hardness was (R^2 = 0.8699): indicating a strong correlation and very strong positive relationship. In the same vein, the coefficient of determination in the case of composites with coarse $CaCO_3$ size and content and shore hardness was (R^2 = 0.6914): indicating a strong correlation and very strong positive relationship**.**

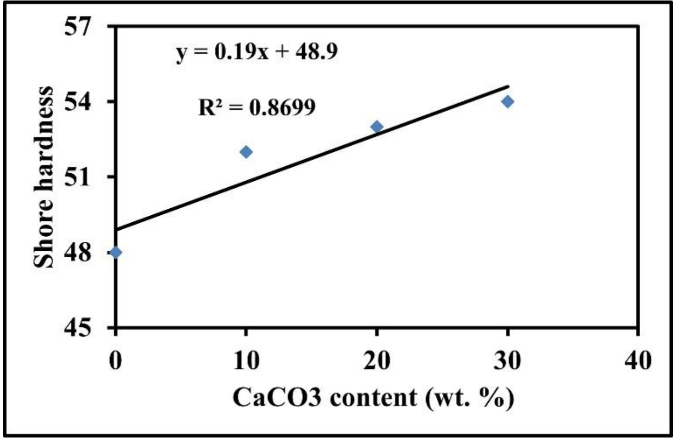

Figure 13: Correlation of size and content of fine $CaCO_3$ with Young’s modulus.

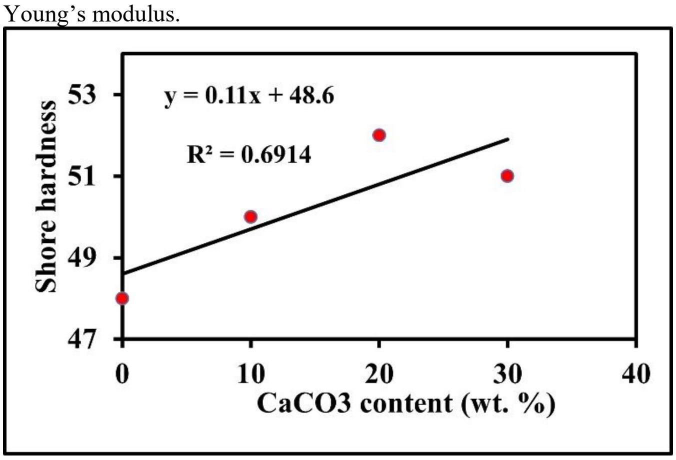

Figure 14: Correlation of size and content of fine $CaCO_3$ with hardness.

5.Conclusion

The effect of size and content of Libyan CaCO3 on the mechanical properties of HDPE were investigated. The results revealed that:

- The average sizes of the coarse and fine $CaCO_3$ particles were 74 nm and 1 nm, respectively.

- The impact strength decreases with the addition of $CaCO_3$. Composites with coarse $CaCO_3$ had higher impact strength than composites with fine $CaCO_3$.

- There is reasonable improvement in the tensile strength after the addition of both fine and coarse $CaCO_3$. With the exception to composites with 30% coarse $CaCO_3$, all HDPE composites showed higher strength than pure HDPE. The tensile strength was higher in the case of fine $CaCO_3$ than in the coarse case.

- Young’s modulus was increased with the increasing the $CaCO_3$ content into HDPE in both cases. The effect of particle size and content of $CaCO_3$ on the young’s modulus was more pronounced in the fine $CaCO_3$ particles than in the case of coarse ones.

- With the exception to the effect of coarse $CaCO_3$ on the tensile strength, the results indicate very strong positive relationships a strong and positive correlation between $CaCO_3$ content and size with all the studied mechanical properties.

- Hardness properties increased with increasing the amount of $CaCO_3$.

- Composites with fine (nano-sized) $CaCO_3$ demonstrated better overall mechanical properties than composites made with coarse $CaCO_3$.

- Libyan $CaCO_3$ can be considered as an excellent reinforcing material for polyethylene since it enhanced its mechanical properties and has the potential to reduce the production cost of these materials.

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