

# Effects of Libyan Kaolin Clay on the Impact Strength Properties of High Density Polyethylene/Clay Nanocomposites

Anour Shebani<sup>1</sup>, Wael Elhrari<sup>1,\*</sup>, Abdalah Klash<sup>1</sup>, Abdelkader Aswei<sup>2</sup>, Khalid Omran<sup>2</sup>, Abdalbary Rhab<sup>1</sup>

<sup>1</sup>Polymer Research Center, Tripoli, Libya

<sup>2</sup>Higher Institute for Comprehensive professions Al garaboulli, Libya

**Abstract** This work aims to investigate the influence of Libyan Kaolin clay on the impact strength properties of high density polyethylene (HDPE)/clay nanocomposites. First, HDPE/clay nanocomposites with various clay content (0, 2, 4, 6, and 8 wt.%) were prepared by melt processing method. The highest impact strength value was observed for nanocomposite with 2 wt.% of clay. Second, HDPE/clay nanocomposites with 2 wt.% clay were prepared and mixed with (2, 4, 6, 8 and 10 wt.%) polyethylene grafted maleic anhydride (PE-g-MA) as a compatibilizer. The effect of PE-g-MA addition was positive and the highest impact strength was observed for nanocomposite with 2 wt.% of PE-g-MA. Third, HDPE/clay nanocomposites with 2 wt.% clay and 2 wt.% PE-g-MA were prepared using different clay particle size. The results show that particle size has considerable effect on the impact strength properties of HDPE/clay nanocomposite. Libyan Kaolin clay acted as reinforcing filler and produced nanocomposites with improved impact strength properties.

**Keywords** HDPE/kaolin nanocomposites, Impact strength, High density polyethylene

## 1. Introduction

Polymer nanocomposites (PNCs) are a class of materials consist of a polymeric substance and a nanoscale reinforcing materials. PNCs are very promising materials for various applications [1]. They are expected to replace polymers, polymer blends, and their traditional composites in parts produced by melt processing techniques. This expectation is justified by the improvements in properties without sacrificing the melt rheological properties [2]. First polymer nanocomposite (PNC) was developed by Toyota Co. (Japan) more than 15 years ago [3]. Since then the field of PNC has grown greatly and hundreds of papers have been published. [4] Substantial improvements in properties such as strength, thermal stability, flame retardancy and gas permeability at very low filler contents as compared to the conventional composites have been reported [4]. Most common used nanoparticles found in the literature used to prepare nanocomposite are nanoclays, carbon nanofibers, carbon nanotubes, nanosilica etc. Nanoclays are the most widely investigated nanoparticles in a variety of different polymer matrices for a wide range of applications [5].

Commercially, a number of polymer/clay nanocomposites

are available [6]. polymer/clay nanocomposites is an interesting and very promising research area due to cost effective, their high specific surface area and their ease of availability from natural resources [7]. Usually property enhancement in nanocomposites occur at very low clay loading (< 5 wt. %) [8]. Much work have been focused on developing polymer/clay nanocomposites using various polymers such as polypropylene (PP) [8], polyamide, polyimide, nylon, polystyrene (PS), ethylene vinyl acetate copolymer, polyethylene terephthalate, polyurethane, low density polyethylene (LDPE) [9], high density polyethylene (HDPE) [10], epoxy [11], blend of PS/HDPE [12], blend of PP/HDPE [13] and blend of PP/LDPE [14]. Number of clay types have been used include Kaolinite (known as kaolin or chain clay), Illite, Bentobite, Chlorite, and Montmonillonte [15, 16]. Among these types of clay, kaolin clay has wide variety of applications in industry, particularly as a filler in paper, plastics, paints and rubber [13]. Kaolin is white, soft, and highly refractory clay. It is mainly composed of fine-grained plate-like particles [9]. It has 1:1 type layered structure, one side of inter layer space is covered with hydroxyl groups of the  $Al_2(OH)_4$  octahedral sheets and other side is covered by oxygen's of the  $SiO_4$  tetrahedral [17]. Due to the fact polyolefin are usually hydrophobic and difficult to adhere with hydrophilic clay particles. Hence, compatibilizers must be introduced in the nanocomposites to improve the dispersion and increase the interfacial interactions between the clay and polymer matrix. Maleic

\* Corresponding author:  
waelelhrari@gmail.com (Wael Elhrari)

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anhydride grafted PP [18], oxidized PP [19], polyethylene grafted maleic anhydride (PE-g-MA) [9], poly acrylic acid [20], vinyl acetate copolymer [21] have been used as compatibilizers in the preparation of polymer/clay nanocomposites.

Properties and utilization of Libyan clay have been studied by many scientists [22-28]. An extensive research work has been carried out in the past years by Industrial Research Center on the natural raw materials from the south of Libya [29]. These researches show that there are many raw materials that can be used in the building industry, one of that materials was kaolin [30]. Other studies have been performed by Petroleum Research Center concerning using local clay as drilling fluid in oil field [31, 32]. In recent years, the properties of calcined clay are widely discussed in cement literature for their pozzolanic properties [29]. Few papers published on using clay as ionic exchange to absorb heavy metal from water [27, 33-35]. However, no attention has been paid to use local clay as reinforcing filler for PNCs.

In this study, the focus was on preparing PNCs with improved impact properties using Libyan kaolin clay from south of Libya (Jarmah Member, Sabha city). Impact properties is one of the most important mechanical properties and an essential part of any materials evaluation [36]. The well documented property advantages that dispersed clay can offer, need to be accompanied by retention of impact strength [37]. On the other hand, the main chemical composition and general properties of Libyan kaolin were reported by Alhadi and Azimah [25]. Libyan kaolin clay can be considered as pure kaolin because its chemical composition is 44-52% SiO<sub>2</sub> and 35-40% Al<sub>2</sub>O<sub>3</sub>, which is close to the value of pure Kaolin (46.5% SiO<sub>2</sub> and 39.5% Al<sub>2</sub>O<sub>3</sub>) that mentioned by Grimshaw [25, 38]. According to Eshmaiel [26] Libyan kaolin clay is relatively high in silica and its physical properties could be referenced as ASTM C618 class. This makes the idea of using Libyan kaolin clay to produce PNCs attractive.

## 2. Experimental

### 2.1. Materials and Methods

High density polyethylene (HDPE) was used as the matrix polymer (SABIC Saudi Arabia, HDPE F00952). The melt flow index (MFI) and density values of HDPE are 0.05 g/10 min (ISO 1133, 190°C, 2.16 kg) and 952 g/cm<sup>3</sup> (ISO 1183), respectively. Maleic anhydride grafted polyethylene (PE-g-MA) prepared in our lab according to reference [38], was used as a compatibilizer. Kaolin is supplied by Industrial Research Center Tripoli (collected from Jarmah Member, Sabha city in Libya). Kaolin was sieved to remove impurities and then passed through different sieves size to get particle size of (< 75, 75-150 and 150-300) µm. Results obtained by Alhadi and Azimah, [25] showed that the plate thickness of this type of kaolin ranges from 26.5 to 40.5 nm.

This is important because nanoparticles are often defined as particles with at least one dimension between 1-100 nm size range [39]. According to others [40], nanoparticles are particles with at least one dimension of less than 1 µm. p-Xylene (Alfa Aesar 99%) was used to melt HDPE before compounded process. The xylene serves to facilitate the melting of the polymer and mixing of the clay particles.

### 2.2. Composite Preparation

HDPE was used as received. kaolin was dried in an air circulating oven at 85°C for 24hr. The HDPE of desire amount was melt in small amount of xylene and then mixed with 2, 4, 6, and 8 wt.% kaolin in a separate bowl. The mixture then dried in an air circulating oven at 85°C for 24hr. Then the final mixing was carried out using twin screw extruder (Brabender) (L/D ratio 48) with screw speed of (70 r.p.m.). The barrel, die temperatures and screw speed were monitored and controlled, as shown in Table 1.

**Table 1.** Temperature and screw speed profiles of the extruder barrel

	Zone 1	Zone 2	Zone 3	Zone 4	Zone 5	Zone 6
Temperature °C	140	160	170	180	190	190
Screw speed (r.p.m)	70					

**Table 2.** Composites composition and codes

Composite code	HDPE wt. %	Clay wt. %	Clay's particle size µm	Compatibilizer wt. %
PE	100	0.0	---	---
PEC1	98	2.0	< 75	---
PEC2	96	4.0	< 75	---
PEC3	94	6.0	< 75	---
PEC4	92	8.0	< 75	---
PEC5	98	2.0	< 75	2.0
PEC6	98	2.0	< 75	4.0
PEC7	98	2.0	< 75	6.0
PEC8	98	2.0	< 75	8.0
PEC9	98	2.0	< 75	10.0
PEC10	98	2.0	75-150	2.0
PEC11	98	2.0	150-300	2.0

The extruded materials were cooled in air and then granules to small pieces. Specimens for impact strength were prepared using injection molding (Xplore 12ml). The same process was used to prepare composites with different amounts of compatibilizers and particle sizes. Details of the composites and codes are reported in Table 2.

### 2.3. Characterization

#### CHARPY Impact Test

The Charpy impact test was carried out to determine the impact strength of the HDPE, and all composite materials using (CEAST Resil Impactor tester), with impact energy of 15 J. The specimens for impact test were prepared and notched according to ASTM (D256-87). Four specimens were tested for HDPE and each composite.

## 3. Results and Discussion

Table 3 shows the impact strength and their standard deviation (STD) of HDPE and all composites. The impact strength of HDPE and composites with no compatibilizers (PE to PEC4) were evaluated with respect to the effect of the clay loading. Virgin HDPE exhibited an impact strength of almost 12 KJm<sup>-2</sup>. This value increased with addition of 2 wt.% clay and then decreased significantly with the addition of 4, 6 and 8 wt.% clay. In general, presence of rigid filler usually deteriorates strength and toughness of polymeric materials [41]. The aggregated clay particles that occurred for the nanocomposites with high clay content (above 2 wt.%) was believed to be responsible for the decrease in impact strength. Increasing clay content causes increase in clay aggregation and decrease in interparticle distance, which lead to lower aspect ratio of clay particle and lower contact surface area, resulting in weak adhesion between polymer matrix and clay, in which subsequently lower their impact strength [42].

**Table 3.** Impact properties values and their STD of PE and all composites

Composite code	Impact strength, KJm <sup>-2</sup>	STD
PE	12.183	1.57
PEC1	16.098	2.42
PEC2	5.922	2.83
PEC3	6.110	1.93
PEC4	8.707	2.51
PEC5	25.025	4.10
PEC6	11.058	1.02
PEC7	9.350	0.74
PEC8	15.675	4.89
PEC9	18.508	5.81
PEC10	39.125	5.34
PEC11	38.851	4.36

In particular, the impact strength of PEC1 is higher than of PE, PEC2, PEC3 and PEC4. This means that 2 wt.% clay has better dispersion in polymer matrix, although there no compatibilizer was used. This improvement can be attributed to the increase in toughness of the composite [12]. Quality dispersion of nanoparticles in matrix also plays key role for an improvement of properties (e.g. impact properties) of

nanocomposites [41-44]. The benefit of the clay as a filler depends on the amount added to the polymer matrix [41]. In general, PNCs exhibit great improvement in mechanical properties, such as strength and stiffness, compared to pure polymers upon addition of minimal amount of nanosize clay particles [45, 46]. Large amount of clay in the polymer matrix tend to limit its use as a filler [43]. Suitable amount of reinforcing clay particles presented in the polymer matrix act as efficient impact absorption agents in the polymer [47].

These results are further illustrated in Figure 1, which shows the effect of kaolin loading on the impact strength of HDPE and composites (PEC1 to PEC4). The PEC1 showed an increase of approximately 25% in the value of impact strength compared to virgin HDPE.

According to Chen and Evans [36], it is well documented and reviewed that the ability of clays to improve the stiffness, strength and resistance to permeation of gases and solvents when added at relatively low levels (< 5 wt.%) to thermosetting and thermoplastic polymers. Anjana and George [13], found that incorporation of nano kaolin clay at 2 wt.% gives maximum improvement in mechanical properties of PP/HDPE blend system. George et al. [12] concluded that tensile strength and tensile modulus is found to increase with 2 wt.% kaolin clay loading, while impact strength is found to increase with 3 wt.% kaolin clay loading in PS/HDPE blend system.

As mentioned earlier, this could be due to the good dispersion of nanoparticles of clay in the polymer matrix. The distribution of the kaolin particles in the polymer matrix could be due to the good aspect ratio of kaolin particles, which lead to increase the impact strength value by increase the filler contact surface with the polymer matrix. However, this variation in impact properties depends mainly on the microstructure and the interface morphology of the composites (including the interfacial bonding, size and spatial distribution of the clay particles into the matrix, as well as the thickness of the interface) [45].

According to the above obtained results, composite with 2 wt.% kaolin clay was selected to study the effect of compatibilization on the impact properties. Therefore, composites with 2 wt.% kaolin and 2, 4, 6, 8 and 10 wt.% of PE-g-MA were prepared. The most widely used compatibilizer is MA grafted polyolefins for the preparation of PNCs [48]. Impact strength and their STDs results of these composites are shown in Table 3 (PEC5- PEC9). When compatibilizer was present, impact strength for 2 wt.% kaolin composites increased. This could be due to the intercalation of PE-g-MA into clay layers helps to expand the clay gallery spacing as well as weaken the interactions between the clay layers, and improve the interaction between polymer matrix and clay particles. Compatibilizers are generally added in the nanocomposites in order to improve the interfacial adhesion between hydrophilic clay and hydrophobic polymer and lead to better mechanical and morphological properties [49, 50]. Incompatibility and weak interfacial interactions hinders the exfoliation/intercalation and preparation of dispersed stable nanocomposite with

improved properties [51].

As shown in Table 3 and Figure 2, the impact strength of PEC5 is higher than of PE, PEC1, PEC6, PEC7, PEC8 and PEC9. PEC5 showed an increase of approximately 108% compared with virgin PE. With the use of compatibilizer, up to 100% increases in impact strength can be reached [52]. Optimum compatibilizer has been proposed in order to achieve a good clay dispersion and mechanical and physical enhancement for the polyolefin nanocomposites [53].

PEC5 (2 wt. % clay and 2 wt. % PE-g-MA) was selected to study the effect of clay particle size on the impact properties of these composites. The size and shape of the clay particles can affect mechanical properties such as

stiffness and tensile and impact strength [53]. The effects of clay particle size on the impact properties are shown in Table 3 and Figure 3.

Maximum impact strength value ( $39.125 \text{ KJm}^{-2}$ ) for the composites was obtained at particle size of  $75\text{-}150 \mu\text{m}$  (PEC10). Composite with particle size of  $150\text{-}300 \mu\text{m}$  (PEC11) exhibited impact strength value ( $38.851 \text{ KJm}^{-2}$ ) close to that of PEC10. The lowest impact strength value ( $16.098 \text{ KJm}^{-2}$ ) for the composites was obtained at particle size of  $< 75 \mu\text{m}$  (PEC1). This implies that particle size has considerable effect on the impact strength properties of HDPE/clay nanocomposite.

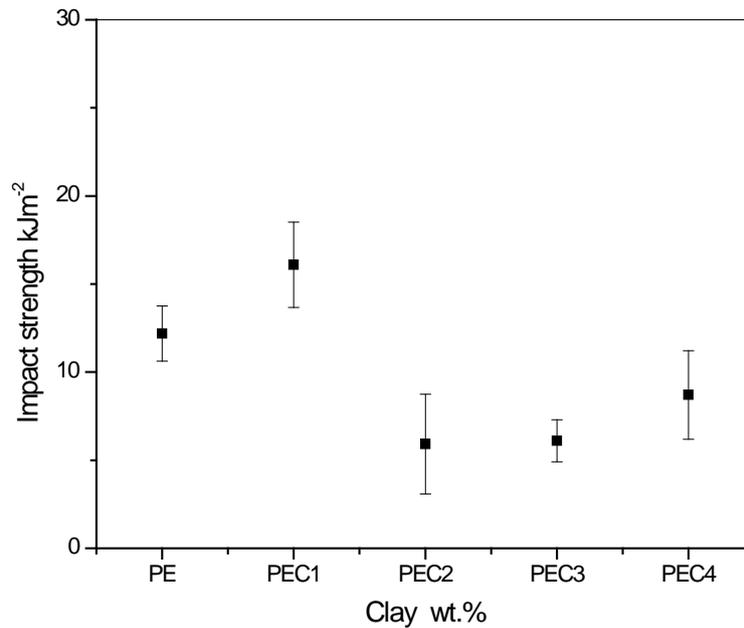


Figure 1. Variation of impact strength with clay loading

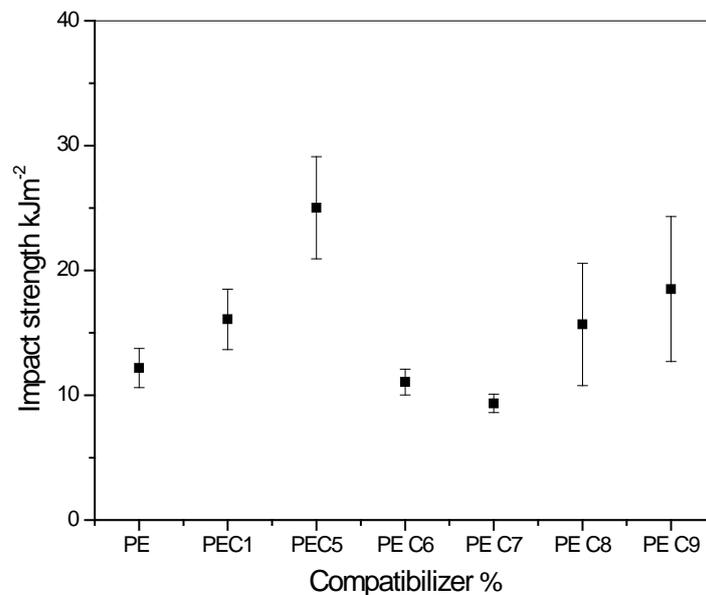
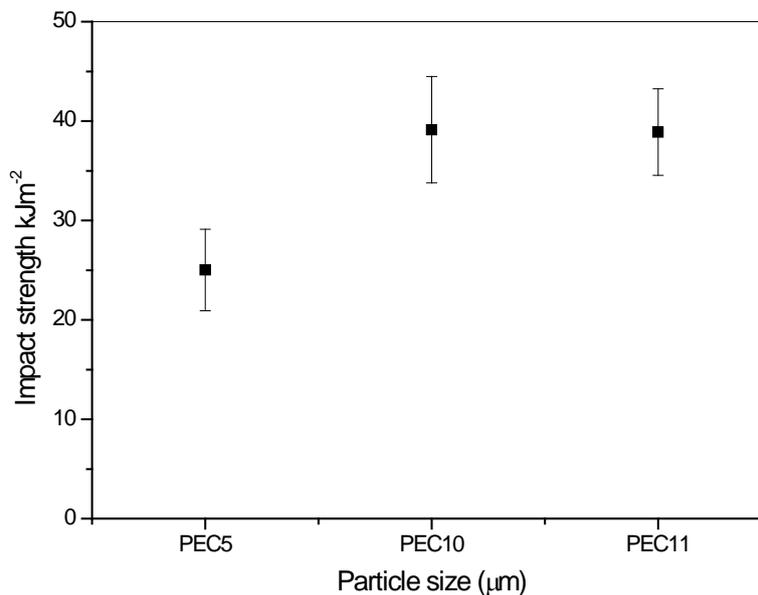


Figure 2. The relation between impact strength of virgin PE and composites (2 wt. % clay load) with (0, 2, 4, 6, 8 and 10 wt. %) compatibilizers



**Figure 3.** Effects of kaolin particle size on the impact strength properties of nanocomposites with 2 wt.% kaolin and 2 wt.% PE-g-MA

Mechanical properties of PNCs can be altered by various factors: properties of the polymer matrix, clay particle size and morphology, particle loading and distribution, interfacial adhesion between clay and matrix, etc. [45]. For high impact and tensile strengths, filler particles need to be of micron size; certainly with as few particles as possible  $> 10 \mu\text{m}$  [53]. Both the larger and smaller particle size seem to have a negative effect on the mechanical properties due to the presence of large individual particle or agglomerates, which act as stress concentrators that trigger the fracture mechanisms [45]. Improper particle size of kaolin at given filler content probably increases the level of stress concentration in the composites with the resultant decrease in impact strength. The proper particle size cannot be predicted, it depends on the particle shape, matrix and particle/matrix adhesion [54].

#### 4. Conclusions

The study shows that Libyan Kaolin can act as inexpensive and effective reinforcing filler for HDPE. The addition of Libyan Kaolin filler has resulted in an improvement in the impact strength properties of HDPE. Maximum improvement in the impact strength properties was obtained at low clay loading (2 wt.%). The impact strength properties is increased to approximately 33% compared to virgin HDPE. The effect of compatibilization was investigated as well. Addition of PE-g-MA increased the impact strength properties. Maximum impact strength value in the composites was obtained with 2 wt.% PE-g-MA. Accurately, additional of 2 wt.% PE-g-MA is found to increase the value of the impact strength of the composite with 2 wt. % clay to approximately 108%. This study covers also the effect of Koalin clay particle sizes on the impact strength properties of HDPE. Kaolin clay with particle size of 75-150  $\mu\text{m}$  produced better impact strength properties

than Kaolin clay with particle sizes of 150-300 and  $< 75 \mu\text{m}$ , respectively, in the composite with 2 wt.% clay and 2 wt.% PE-g-MA.

It must be concluded that the improvement in the impact strength properties can be related to a good dispersion of clay particles in the polymer matrix. This can be achieved through the optimizations of clay loading, compatibilizers and clay particle size. It must be also concluded that it is possible to produce nanocomposites with Libyan kaolin clay without scarifying the impact properties. Therefore, more attention needs to be given to other mechanical and thermal properties in next studies. We consider that the improvements in composites properties have never reached to the end.

We believe that the obtained results will encourage Libyan scientists to start using of Libyan kaolin clay and other clays in the field of nanocomposites. We also believe that this attempt will open the door for using domestic clay to produce PNCs with superior mechanical properties and encourage the domestic industries to manufacture PNCs on commercial scale in the future.

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