The use of ground & ultrasonicated dolomite (GUD) for improving the tensile performance of Poly (ethylene-co-vinyl acetate) copolymer composite

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Abstract. The combination of the organic and inorganic materials to fabricate a new form of material called ‘composite’ has been performed since several decades ago. However, the strategy to improve the homogeneity of the resultant composite system is still being the main focus of current research. In this study, dolomite and poly (ethylene-co-vinyl acetate) (PEVAc) were employed as filler and matrix, respectively. Dolomite was ground and ultrasonicated before being used as filler. It can be observed that the size of dolomite particles has been reduced significantly upon the grinding and ultrasonication processes. The effect of ground and ultrasonicated dolomite (GUD) addition on the mechanical performance of the PEVAc copolymer was investigated. Results indicate that the GUD filler has successfully increased the tensile strength, elongation at break, modulus of elasticity and tensile toughness of the PEVAc copolymer when being employed in 1 wt%. However, the use of higher content of GUD resulted in the decreasing trend of those properties. This shows that the ground and ultrasonicated dolomite with smaller and higher surface area particles than its pristine form could bring improvement to the mechanical performance of the copolymer when being used in low loading as it can be more easily dispersed in the copolymer matrix.

1 Introduction

Poly (ethylene-co-vinyl acetate) (PEVAc) is a random copolymer composed of semi-crystalline polyethylene (PE) and amorphous vinyl acetate (VAc) as the monomer. PEVAc has high flexibility properties contributed by the amorphous structure of the VAc phase [1,2].

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Their physical and mechanical properties depend on their VAc content. The higher the VAc content the softer and rubberier the polymer. PEVAc is widely utilized in shoes, food packaging, adhesive and medical application [3,4]. In this research, PEVAc is aimed to be used in medical applications especially in implantable biomedical devices. Basically, PEVAc has low tensile strength but to be employed in implantable biomedical devices, the tensile strength of the PEVAc should be improved while maintaining their flexibility. Commonly, the inorganic filler is utilized to improve the tensile properties of the PEVAc due to its reinforcing capability, durability and thermal stability. In this research, an inorganic mineral filler, dolomite was employed to improve the tensile properties of the PEVAc copolymer.

Dolomite is a carbonate rock that composes mainly of dolomite minerals. It is widely scattered in nature in several countries. In Malaysia, Perlis and Perak were reported to have abundant dolomite with large quarries [5-7]. Perlis Dolomite is also said to possess a great quality of mineral rock powder [8]. Dolomite has the chemical composition of CaMg(CO3)2. Dolomite structure resembles calcite structure by having a double carbonate structure. However, dolomite has a crystal lattice of double carbonate with alternating Calcium (Ca) and Magnesium (Mg) ion while calcite only has Calcium ions. It also has a trigonal rhombohedral system.

Dolomite is employed in many industries such as pharmaceutical, fertilizer, paint, paper, glass, cement and construction [7,8]. Recently, dolomite is found to be used as filler in polymer composite. This is due to their properties; high hardness which suit to improve the hardness of a polymer. In addition, dolomite is also inexpensive and affordable. Several researchers reported using dolomite as filler in polymer composites for the purpose of increasing the mechanical properties of the host polymer [9-12]. Ahmad Saidi et al. (2018) reported that the tensile strength of the PBT/dolomite increased as dolomite was added up to 10% loading [9]. Another research by Syed Bakar et al. (2013) also reported that the tensile strength of the rPP increased with the addition of dolomite [10]. However, some researchers found out that the mechanical performance of the host polymer decreased with increasing dolomite loading. Mohd Din et al. (2018) reported that the tensile strength of the PP/dolomite decreased as dolomite was added and further decreased as filler loading increased [11]. Adesakin et al. (2013) also reported having the same result where the tensile strength of the polyester decreased as dolomite was added [12]. This might be due to the poor dolomite distribution in polymer and poor interfacial adhesion between filler and host polymer. Poor filler distribution might due to the agglomeration of filler at high filler loading. Large particle size of filler could also be the reason for poor mechanical performance of the resultant composite material [11, 12]. Consequently, researchers are proposing the use of submicron and nano-size fillers having greater dispersing ability and large surface area to provide more efficient reinforcing phase for polymer composite system.

Normally, pristine dolomite comes in various particle sizes (>200 µm) and to ensure well dispersion of dolomite in polymer, the size of dolomite should be reduced. Several researchers reported methods to reduce dolomite size. Commonly, mechanical milling was introduced for size reduction purpose. There are several grinding millings employed such as vibration milling, attritors, mixers and planetary milling. This milling involves the mechanical breakdown of large solid into smaller particles size without changing their chemical structure. Nik Adik et al. (2016) found out that the milling time affects the size reduction of dolomite. Dolomite size was reduced to submicron size after grinding for 2 to 5 hours [13]. Tengku Mustafa et al. (2015) suggest that grinding process of dolomite can increase its particles’ fineness and decrease its crystallite size. However, dolomite tends to agglomerate at a longer milling time [8]. Therefore, in this research, ultrasonication procedure was introduced after the milling process to reduce the agglomeration effect. Previous researches indicate that during the ultrasonication process, waves are propagating into the particle through a liquid medium. Thus, it forms the alternating high- and low-
pressure cycles. During the low-pressure cycles; high-intensity sonic waves create a large number of microbubbles which later collapse during the high-pressure cycles in a very short time which is called ultrasonic cavitation. These can cause high local temperature, high speed impinging liquid jets and strong hydrodynamic shear-forces. De-agglomeration of particles can be achieved through these effects [14-16]. Thus, large particles size due to agglomeration can be reduced. This article focuses on how the smaller filler size dolomite and dolomite loading affect the tensile performance of the PEVAc composite.

2 Methodology

In this research, dolomite was supplied by Perlis Dolomite Industries. Polyethylene-co-vinyl acetate (PEVAc) copolymer with 25 wt.% vinyl acetate composition was supplied by Sigma Aldrich. Dolomite with particle size of 150 µm was ground for 6 hours with 500 rpm speed by using Fritsch Pulverisette planetary mill. Dolomite was ground with 50 pieces of grinding ball of 15 mm diameter and mass of 13.78g each. Then, it was ultrasonicated by using Branson Digital Ultrasonic Disrupter /Homogenizer (Model 450 D) for 2 hours at 30% amplitude with pulse on time 10s and pulse off time 10s. The ground sample (GD) and the ground and ultrasonic sample (GUD) were analyzed by scanning electron microscopy (SEM). GUD dolomite was employed as filler for PEVAc composite and the composite's performance was studied based on their tensile properties. The PEVAc composites were prepared using melt compounding method by heated two roll mill machine with 1 wt.%, 3 wt.% and 5 wt.% of dolomite loading. Then, the compounding was compressed into a thin film with a thickness of 1mm by using a compression molding machine (GOTECH CO model GT-7014-H30C). Lastly, the hardened sample was cut into dumbbell shape for tensile testing.

2.1 Scanning Electron Microscope (SEM) Analysis

Morphological analysis by SEM was done on the ground dolomite (GD) and ground and ultrasonicated dolomite (GUD). It was performed to compare the size of dolomite before and after being ground and ultrasonicated. Scanning Electron Microscope (SEM), model SEM-JEOL JSM-6010LV with 10kV voltage was employed and the images were captured with magnification of X500.

2.2 Tensile Test

The virgin PEVAc and PEVAc composites were evaluated and compared based on their tensile properties. The samples were cut according to ASTM D-638-M-5 to obtain standard size dumbbell specimens. The tensile test was done by using Instron machine model-5582 with a crosshead speed of 50 mm/min. The mean values of tensile strength, elongation at break, tensile toughness and Young's modulus were recorded. The tensile toughness value was obtained by measuring the area under the stress-strain graph.

3 Result and Discussion

3.1 Morphology of The Ground Dolomite (GD) / Ground and Ultrasonicated Dolomite (GUD).

The size of the ground dolomite (GD) and ground + ultrasonicated (GUD) was observed and compared through the obtained SEM images. Based on Fig. 1, the SEM image shows that the
size of dolomite reduced significantly as it was ultrasonicated for 2 hours. As mentioned earlier, ultrasonic cavitation and strong hydrodynamic shear-forces can cause de-agglomeration of dolomite and reduction in its particle size.

Fig. 1. SEM images of a) Ground dolomite (GD) and b) Ground and ultrasonicated dolomite (GUD)

3.2 Tensile Properties of the Virgin PEVAc and PEVAc composites

The PEVAc copolymer was reinforced with different loading of GUD filler and the tensile performance of the resultant composites was studied. Fig 2 summarizes the tensile strength, elongation at break, modulus of elasticity and tensile toughness of the virgin PEVAc and PEVAc composite with different GUD loading (1%, 3% and 5%). As shown in Fig 2a) the tensile strength, elongation at break and tensile toughness of the host PEVAc have been improved with the addition of GUD in the loading of 1 to 5 wt.%. Among all, the PEVAc composite with GUD loading of 1 wt.% has the highest tensile strength with an increment of 26% as opposed to the virgin PEVAc. This indicates that when added in 1 wt.%, the GUD can serve as the best reinforcing filler for the PEVAc copolymer. When added in low loading, the GUD particles can easily be dispersed during the compounding process. It is well understood that when the filler is well dispersed in the polymer matrix, it will develop good interfacial interaction with the matrix [1, 5, 11]. As a result, enhancement in the tensile properties of the matrix is more significant. However, the tensile strength of the PEVAc composite decreases with increasing filler loading. PEVAc with 5% of dolomite loading has the lowest tensile strength which is 7.4 MPa, which exhibits a decrease for about 7 % compared to the PEVAc composite with 3% filler. This might due to the excess GUD filler content in the PEVAc matrix. This may cause overcrowding and agglomeration of GUD particles that hinders good dispersion and distribution of the filler throughout the copolymer matrix. Poor dispersion of GUD filler retard the stress transfer mechanism from the filler to the matrix, thus lowering in the tensile strength of the composite could be observed. The excess GUD might as well incompatible with the polyethylene (hydrophobic) phase of the PEVAc copolymer, as this mineral filler is the hydrophilic material. Thus, poor matrix-filler interaction caused a decrement in tensile strength value.

Interestingly, the elongation at break of the PEVAc composite shows the same trend as tensile strength which PEVAc composite has a higher elongation at break value when compared to the pure PEVAc. Ghada et al. (2010) also show the same elongation at break trend where composite has higher elongation at break value when compared to the virgin matrix [17]. As seen in Fig 2b) The PEVAc/GUD composite with 1 wt.% GUD loading has the highest value with an increment of 25% when compared to the virgin PEVAc. This improvement might be due to homogeneous dolomite dispersion in the PEVAc matrix. Other researchers also stated that use of smaller size filler can more potentially produce the
composite with homogeneous structure, with good dispersion of filler in the matrix phase [18]. The homogeneous distribution of filler also allows the stretching of matrix into greater extent before it breaks under tension load. However, as the GUD loading increased the elongation at break of the composite decreased. The elongation at break values of the PEVAc/GUD 3% and PEVAc/GUD 5% were reduced by 2% and 1.7%, respectively when compared to the PEVAc/GUD 1% composite. As mentioned earlier, at higher GUD loading agglomeration of filler may occur and creating an inhomogeneous composite. The agglomerated particles hindered the mobility of the copolymer chains, thus lowering the flexibility of the matrix.

Apparently, the tensile toughness of the PEVAc composite was higher when compared to the virgin PEVAc. PEVAc/GUD composite with 1 wt.% GUD composition has the highest tensile toughness value with an increment of 41% when compared to the virgin PEVAc. As previously mentioned, GUD has underwent size reduction and de-agglomeration processes before being used as filler. This makes GUD an “easier to disperse” filler for the production of homogeneous composite. When this small size filler embedded in the matrix phase, it allows the molecular motion of the copolymer chains, and at the same time helps to transfer the stress throughout the matrix phase. These allow the energy absorption mechanism during tensile deformation, in which can avoid sudden break or failure. Thus, an increase in the composite’s tensile toughness can be observed. However, as the GUD loading increases their tensile toughness is decreases. Reverse effects caused by overcrowding of GUD particles were the cause of this phenomenon.

Fig 2d) shows that the modulus of elasticity of the PEVAc could be improved with low loading of GUD filler (1 wt.%). As mentioned earlier, the GUD can be more homogeneously dispersed in the matrix when added in low content. Thus, GUD at 1 wt.% developed good interfacial interaction with the matrix. Stiffening of the matrix is possible. However, when the GUD loading was increased, poor filler-matrix interactions led to the inefficiency of the filler in stiffening the matrix [19]. As a result, the modulus values of the PEVAc/GUD 3% and PEVAc/GUD 5% were decreased by 6.49% and 22.58%, respectively when compared to the PEVAc/GUD 1% composite.
Fig. 2. The a) Tensile strength, b) Elongation at break, c) Tensile toughness and d) Modulus of elasticity of pure PEVAc and PEVAc composite

4 Conclusion

Based on the SEM analysis, it is clearly seen that the size of dolomite particles that have been ground and ultrasonicated was much smaller when compared to those that have been ground only. This particle size reduction can facilitate the dolomite dispersion in the PEVAc matrix. Therefore, the dolomite that has been ground and ultrasonicated (GUD) was utilized as filler for the production of the PEVAc composite. The mechanical performance of the composites was studied in terms of tensile properties. Overall, the PEVAc composites show greater tensile strength, elongation at break and tensile toughness when compared to the pure PEVAc. However, as the GUD filler loading increased from 1 wt% to 5 wt%, the tensile strength, elongation at break and tensile toughness decreased due to agglomeration of GUD particles at higher filler loadings. It can be concluded that the GUD filler loading affects the mechanical performance of the PEVAc composite.

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