EFFECTS OF GRAPHITE MILLING TIME AND COMPOSITION TO TENSILE PROPERTIES OF POLY-METHYL METHACRYLATE (PMMA)/GRAPHITE COMPOSITE

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Abstract: Effects of milled graphite composition on the mechanical, surface chemistry and morphological properties of poly-methyl methacrylate (PMMA)/graphite composite were investigated. Milling under atmospheric condition showed small reduction of crystallite size but still preserving the crystalline phase of graphite particles. In addition, it had been observed that the particle size had reduced from 25.65μm to 6.49μm after 50 hours of milling. The composites showed an X-ray diffraction peak and functional group become obvious with higher graphite composition exists in the composites. Overall, modulus of elasticity was improved by the addition of milled graphite. It reached the maximum level when the addition of milled graphite content is 2wt. %, and the highest value of modulus of elasticity recorded at 1421.77 N/mm^2 was at 2 wt. % of 50 hours milled graphite content. However, it experienced a decreased when the milled graphite content was added to 3wt. %. This is due to the poor interfacial bonding between the polymer matrix and milled graphite filler. The electron microscopy images revealed that the occurrence of agglomeration of graphite particles in the PMMA matrix. This phenomenon showed that the poor dispersion of graphite in the polymer matrix resulting in the decrease of modulus of elasticity of PMMA/graphite composites at 3wt.% and 4wt.% of milled graphite content.

Keywords: Mechanical milling, graphite/polymer composite, elastic properties.

Introduction

Polymer matrix composites (PMC) are a common advanced composite in which the polymers being reinforced into secondary phase production, such as glass, fibre, particles and flakes. PMCs have attractive facets as they are lighter, stronger, and stiffer than unreinforced polymers or conventional metal, with the advantage that their properties and form can be tailor-made to meet the needs of specific applications. The addition of nano-particles to a polymer matrix has proven to be an effective mechanism to enhance polymer matrix properties. Dispersion of nano-sized fillers improve matrix strength, modulus, thermal stability, impact resistance, barrier performance, and conductivity.

In recent years, increase attention has been devoted to developing polymer-graphite composites for application where electrical or thermal conductivity is required (Krupa *et al.*, 2001). As naturally abundant graphite is a well-known material for its advantage in mechanical, electrical, and thermal properties. Additionally, it offers a great opportunity for producing multifunctional composites in a cost-effective way (Lau *et al.*, 2009).

In the processes of manufacturing polymer composites, short fibre or powder type fillers are added into the polymer matrix mixture to obtain appropriate mechanical and electrical material properties (Lee *et al.*, 2006). Any of the additions, used as reinforcement for the composites should have good material properties as well as suitable shapes. The combination of film casting and injection moulding in the fabrication process are capable of increasing the mechanical in the material properties. The polymer matrix used in

this study is poly methyl methacrylate (PMMA). PMMA shows good material characteristics, such as colourless transparency, and good colouration attribute. A good dispersion of graphite in polymer matrix can be improved by certain chemical or physical modification to the graphite (Xiao *et al.*, 2002). There are known several methods in which graphite particles are able to be dispersed homogeneously in a continuous polymer matrix, however due to their infusion incompatibility it is difficult to be done (Mo *et al.*, 2005). Therefore, ball milling was later introduced to obtain smaller graphite particle size.

It has been proven that ball milling is one of the effective ways to produce *carbon nanostructures*. Extensive investigations had been performed to characterise the nanostructure and properties of ball-milled natural graphite (Yue *et al.*, 2009). Conventional milling resulted in some ribbons comprised of graphene planes with defects, delamination, translation, warping and curvature (Welham *et al.*, 2003). Instead, ball milling could produce highly curved graphene planes, forming various carbon nanostructures such as carbon nanoarches and graphene nanoplatelets (Knieke *et al.*, 2010; Jeon *et al.*, 2015).

Over the years, more extensive investigations had been ensued on PMC with carbon-based materials into nanoscale especially in producing carbon nanotubes (CNTs), since carbon-based materials became important early in the century. The production of CNT, despite its promise in manoeuvring various functionalities, is still expensive at present for any widespread composite applications (Wong *et al.*, 2006). Consequently, graphite is a potential alternative to CNTs with regards to the cost and desired properties.

Single wall carbon nanotubes (SWNT), multiwall carbon nanotubes (MWNT), as well as carbon nanofibers (CNF) are being used for reinforcing polymer matrices for improved mechanical, thermal, and electrical properties (Zeng *et al.*, 2004). While tensile strength and elongation were slightly reduced by the presence of CNF's in the PMMA matrix, fibre tensile modulus increased by more than 50%, and compressive strength was more than doubled by the addition of 5 wt. % CNF. The loading conditions, which include the test temperature, strain rate, and fracture behaviour under various stress states, are also related to the mechanical properties (Cheng & Chen, 2004).

The scope of this research is to characterised the properties of ball-milled graphite and further determine the effect of mechanical milled graphite, the reinforcing material on the mechanical properties, surface chemistry and the morphology of PMC; which was produced by PMMA and milled graphite by the *solution casting method*. Various instruments such as Fourier transform infrared (FTIR) spectroscopy, scanning electron microscope (SEM), X-ray diffraction (XRD) and universal testing machine (UTM) were utilised to test and analyse the PMC samples.

Materials and Methods

Graphite being used was supplied by R&M Chemical, which has average particle size of less than 50μm, 99.5% purity and bulk density value between 20-30 g/100ml. PMMA and chloroform were purchased from Sigma-Aldrich.

Milling of Graphite

The ball milling experiment was carried out at room temperature in a Retsch, PM100 planetary ball milling apparatus. The process of ball milling was conducted for 10, 20, 30, 40 and 50 hours in this research, to identify the effect of different milling time to any structural changes of milled graphite. Before the milling, the graphite was weighed according to the ball-to-powder weight ratio (BPR) of 10:1 with speed of 120 rpm and this process was repeated until reaching the desired milling time. The structural change and crystalline structure of the graphite after milling was determined by X-ray diffraction spectrometer (XRD) of model Rigaku Mini Flex II. Scanning electron microscopy (SEM),

model JEOL JSM-6360LA was used to observe the morphologies of the ball milled graphite for the different milling time. SEM analysis was performed after various milling time under an air atmosphere.

Polymer Composite Fabrication and Characterization

The fabricating of test samples were done by blending PMMA with the powder of ball milled graphite. The milled samples used for this process were for the milling time of 10, 30 and 50 hours which was collected in the first stage. Solution casting method was used in this experiment to prepare the PMMA/ graphite composite, 2.0 g of PMMA which had been dissolved in a 20 ml of chloroform concentration. Then, graphite powder with an amount of 1 wt. % was later being added into the PMMA solution. The mixture between PMMA and graphite powder was dispersed in ultrasonic agitation by blasting ultrasonic bath for one hour, and the mixture was then poured into petri dish. The admixture was then being left dried under room temperature for five days in order to allow the solvent to evaporate for a firm casting process result. By repeating the procedures

above, the samples were prepared in 2, 3 and 4 wt. % of milled of graphite. The tensile test are done to the samples by using universal tensile machine (UTM), model M350-10 CT.

Results and Discussion

Milled Graphite

Figure 1(a) and are the SEM images of un-milled graphite and milled graphite that has been milled for (b) 20 hours and (d) 50 hours. Graphite particles have a flaky appearance with sharp edges and after 50 hours of milling time, the graphite particles decrease gradually and it is highly layered and flat. The particle size has reduced from 25.65 μm to 6.49μm. This indicates that the ball milling leads primarily to size reduction by fracture of the larger particles (Welham *et al*., 2003). This also reveals that the graphite particles are still having high crystallinity after milling under air atmosphere for 50 hours. Additionally, the edges of these flat plates are more rounded than the starting material (unmilled graphite), suggesting severe oxidation had occurred during the ball-milling process (Ong & Yang, 2000). Figure 1 (b) shows SEM images of pure PMMA that has a clear and smooth surface.
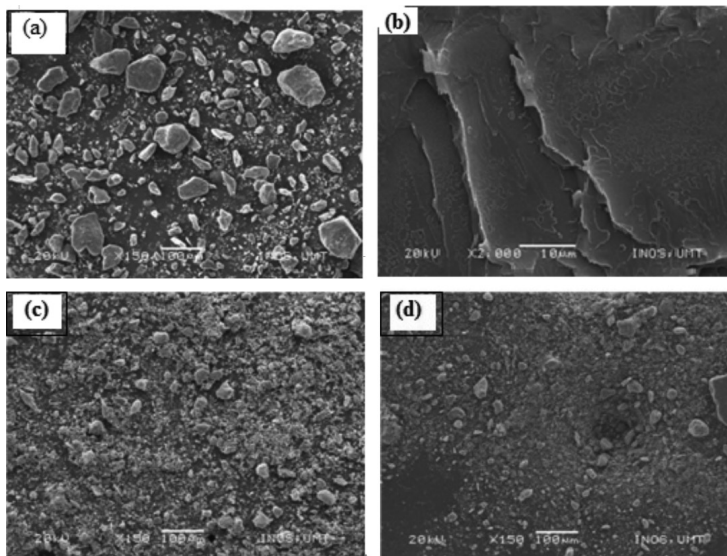

Figure 1: SEM micrograph of (a) unmilled graphite, (b) pure PMMA, (c) 10 hours and (d) 50 hours of milled graphite.

Figure 2, showed that the intensity of (0 0 2) peak decreases with increase of milling time, and reaches a weakest point at about 20 hours milling, while interestingly increases subsequently at long-term milling, such as longer than 30 hours. It was found that the three-dimension (3D) orders of crystalline graphite powders are destroyed during the milling process (Tang *et al*., 2009). Samples that have been milled for a long period of time do not result in an amorphous phase alike that of milled process in argon, nitrogen, hydrogen or vacuum atmosphere (Kuga *et al*., 2002), but they form a better ordered crystalline structure in the prolonged grinding.
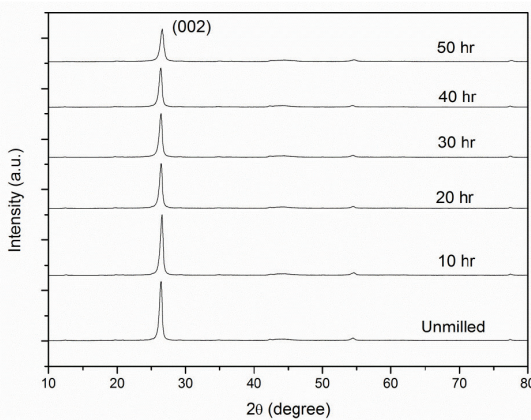

Figure 2: XRD pattern of unmilled and milled graphite from 10 to 50 hours.

Apart from the intensity, there is no significant change in the profile of the diffraction peaks obtained from the starting material (unmilled graphite) and samples that been milled up to 50 hrs. This reveals that the crystallinity of graphite milled in a planetary mill still preserve the crystalline phase of raw materials (Tang *et al*., 2009). The crystallite thickness (Lc) of graphite milled up to 50 hours is illustrated in Figure 3. The crystallite thickness reported is calculated using Equation (1), which is the Scherrer equation (Yue *et al*., 2009)

$$L_c = \frac{K\,\lambda}{\beta\,cos\,\theta} \qquad (1)$$

Where, λ is the X-ray wavelength in the Kα band for Cu (0.154 nm), K is a function of the crystallite shape, θ is an angle of incidence and β is the full width at half the maximum diffraction peak (FHWM), respectively. From the X-ray diffraction data, the crystallite size was found to decrease gradually with the increasing of milling time, from 17.62 nm to approximately 15.00 nm.

In mechanical milling, graphite is placed together with some milling balls in a vial. Milling balls, which are also known as charge materials, are then moved in the vial upon the motion of the vial. The reason to move the charge materials is to bring them in colliding positions. Subsequently, the collision created impact between the charge materials. The
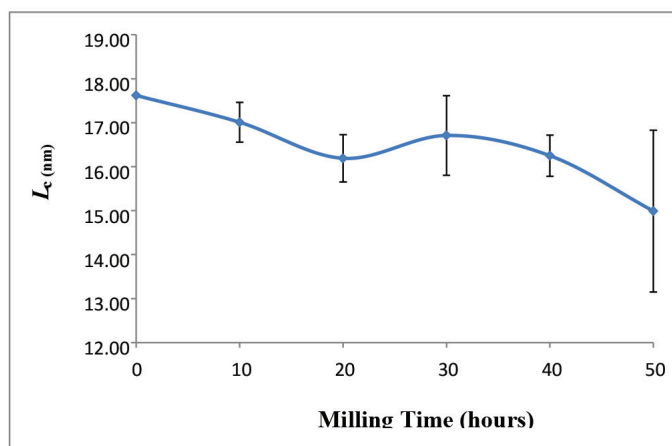

Figure 3: Crystallite thickness of milled graphite with various milling time.

energy generated during impact is expected to be the source of crack propagation and fracture leading to the breakage of the work materials into smaller sizes. The higher the impact energy, the smaller the size of the fragments produced (Budin *et al*., 2009). A simulation work to study the impact energy of the balls to the rate of size reduction in planetary ball mill has showed that the size reduction behaviour was correlated with the balls' impact energy (Misra, 2003; Chen *et al*., 2005).

Characterization of PMMA/graphite Composite

Figure 4 show the XRD patterns of PMMA/ graphite composite for 50 hours milled graphite with different concentration of graphite powder. The pure PMMA is also shown in the figures for comparison. While pure PMMA shows a broad peak (amorphous phase), the PMMA/graphite composites show a sharp peak approximately at $2\theta = 26.45°$ which correspond to a d spacing of 3.37Å that correspond to the characteristic peak of pure graphite. Therefore, the occurrence of peaks confirms not only the presence of graphite, but also the fact that the graphite powders are still in order after various milling time and consist of multilayer of graphite structures and thus maintain their original d-spacing (Yasmin *et al*., 2006).

However, the less intense peaks observed in the figures indicate the uniform dispersion of graphite powder. Moreover, the 4 wt. % graphite/PMMA composite shows a more pronounced peak than the 3 wt. %, 2 wt. % and 1 wt. % graphite/PMMA composites. The higher intensity for higher graphite content can be attributed to the higher graphite layers. It shows that there is significant amount of graphite particle in the composites that can be detected by XRD.

The stress-strain curve is a graphical representation of the relationship between stress, which is derived from measuring the load applied on the sample, and strain, which is derived from measuring the deformation of the sample, such as elongation. Figure 5 display the stress-strain curves of PMMA/graphite composite for 3 wt. % of graphite of 50 hours milled graphite measured for 3 times of tensile stress. Figure 6 depicts the modulus of elasticity for PMMA/graphite composite between 0 to 4wt. % of unmilled graphite, 10 hours, 30 hours and 50 hours milling of graphite.

It shows that the modulus of elasticity reaches the maximum value when the graphite content in PMMA/graphite composite is 2 wt. %. On the other hand, the modulus of elasticity for PMC with 3 wt. % and 4 wt. % of graphite content show a decreased in the aft. Among these graphs, the PMMA/graphite composite with 50 hours milled graphite shows the highest modulus of elasticity. The modulus of elasticity for 1 wt. %, 2 wt. %, 3 wt. % and 4 wt. % are 1383.53 N/mm², 1421.77 N/mm², 1464.51 N/mm² and 1237.42 N/mm², respectively.

Dispersion of graphite is important to the variation of mechanical properties of the composites. In this study, the decrease in modulus of elasticity is probably due to low dispersity of graphite in the polymer matrix. Since the dissolved PMMA have higher viscosity, it would be difficult for graphite particles to disperse efficiently (Lee *et al*., 2006). The modulus of elasticity for PMC with 50 hours milling of graphite increases until 3 wt. % of graphite in the PMC. The reduction of particles size with higher miling time is able to increase plastic deformation and creates structural deformations. This comminution that containing functional groups forming the bonding between graphite and polmer molecule. With the higher milling time sample, it can contribute to the better elasticity with higher milled graphite concentration (Abdullah *et al*., 2019) .This suggests that the mechanical milling which breaks the larger particles into finer size does have effect on mechanical properties by providing better dispersion of graphite in the polymer matrix.
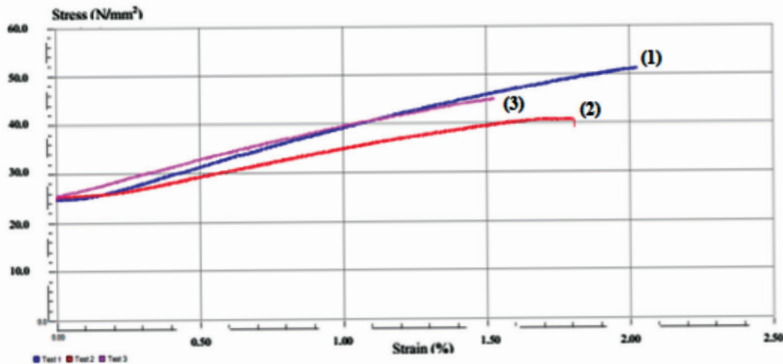
Figure 5: Stress-strain curve of PMMA/graphite composite with 3 wt. % of 50 hours milled graphite.
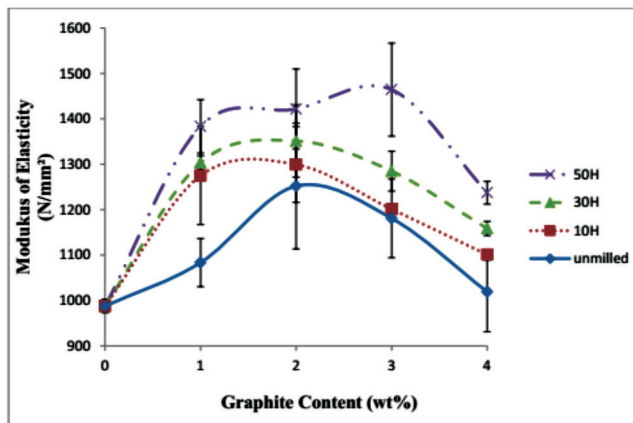

Figure 6: Modulus of elasticity for unmilled, 10 hours, 30 hours and 50 hours milling with different graphite wt. % in PMC.

Conclusion

The SEM images proved that the mechanical milling processes leads to size reduction by breaking the larger particles. The crystalline phase of graphite was still preserved after various milling time in the air. On the other hand, the PMMA/graphite composites showed a sharp peak approximately at $2 = 26.45$ which corresponds to the characteristic peak of pure graphite, indicating the existence of graphite in the PMC. With the information provided by XRD pattern, it was found that the crystallite size had reduced approximately 15 %, from 17.62 nm to 15.00 nm after 50 hours of milling process. The modulus of elasticity was improved by the addition of milled graphite content. It shows the highest value of modulus of elasticity, 1421.77 N/mm² at 2 wt. % of 50 hours milled graphite content. However, the modulus of elasticity decreased when the milled graphite content was added to 3 wt. %. This is due to the poor interfacial bonding between the polymer matrix and the milled graphite filler. The high viscosity of PMMA also hinders the agglomeration of graphite particle from dispersing effectively. From the results obtained, it shows that the smaller the particle size of graphite, the higher the value of modulus of elasticity. This concludes that the mechanical milling which breaks the graphite particle into finer size does have effect on the mechanical properties.

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