Thermal Degradation of Nanocomposited PMMA/TiO$_2$ Nanocomposites

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Abstract. The polymer nanocomposite is a new choice to conventionally filled polymers. The lack of proper binding between the filler and the polymer can lead the decrease of the thermal and other properties of the nanocomposites. In this study, the nanocomposited PMMA/TiO$_2$ nanocomposites were prepared using sonication and solution casting method at different weight percent TiO$_2$. The aims of adding TiO$_2$ in the PMMA is to study the effects of TiO$_2$ nanofiller on the thermal properties nanocomposites. FESEM results show the higher amounts of TiO$_2$ in PMMA increase the rough surface morphology of the samples. Further, the Raman results reveal that the TiO$_2$ nanofiller were successfully intercalated into the PMMA matrix. In addition, the thermal properties of nanocomposited PMMA/TiO$_2$ nanocomposites were increased with the addition of TiO$_2$ in the PMMA.

1. Introduction

In recent years, there has been a strong prominence on the development of the polymeric nanocomposites and the interest in the production of them has comes from the large variety of possible applications including this type of material. The features such as higher resistances towards high temperature, UV radiation, high gas impermeability, higher mechanical strength, low expansibility and processing flexibility can be achieved by the production of the polymer nanocomposites. The particulate composites reinforced with the micro or nanosized particles of various materials are the most commonly utilized composites in everyday materials. Particles are normally added to increase the matrix elastic modulus and also yield strength. Therefore, by scaling the particle size down to the nanometer scale, it has been proven that the novel material properties could be obtained. Further, the
polymer filled with the nano-sized fillers exhibit a dramatic improvements in the mechanical, thermal and also flammability properties [1]. Many previous studies have been reported on the properties of the nanocomposites. A. Laachachi et al has mix the poly (methyl methacrylate) with the TiO$_2$ by molten the PMMA pellets and the filers using a rheometer at 225 °C and 50 rpm. The resulting composites then were pelletized using rotary cutter mill and moulded by compression. From the results, they found that the nanoparticles of TiO$_2$ are well distributed in the material with some tendency to aggregation and the TiO$_2$ nanoparticles significantly enhance the thermal stability of PMMA which attributed to the restriction of mobility of polymers chain confirmed by the increase of the thermal properties with the TiO$_2$ amount [2]. Further, the researcher has prepared the nanocomposite by coating method. In the study, they found the problem in coating PMMA and TiO$_2$ which is lack of proper binding sites on the surface that can leads in the bad adhesion and hence, can cause the weak properties of the sample [3]. In the literature, the presence of inorganic nanoparticles can help to an increase of thermal properties of the materials [4-7]. Therefore, in this study, the polymer PMMA was added with the TiO$_2$ nanopowder to study the thermal properties and thermal degradations of the nanocomposited PMMA/TiO$_2$ nanocomposites at different weight percent of TiO$_2$. The samples were prepared using the sonication and solution casting method and the samples were measured using field emission scanning electron microscopy (FESEM), Raman spectroscopy and thermogravimetry analysis (TGA).

2. Experimental Procedure

There are several steps involve in the preparation of PMMA/TiO$_2$ nanocomposites. First, the preparation of the PMMA and TiO$_2$ solution where beaker A contain of 0.6 g poly(methyl methacrylate) (PMMA) (by ChemAR) with 10 ml toluene, and beaker B contain of 1 wt% of titanium dioxide (TiO$_2$) nanopowder (by ALDRICH Chemicals) with 10 ml toluene. Both of the beaker A and B were sonicated for 30 min. Then, the solution in the beaker A and B were mixed together and was sonicated again for 1 hr. After that, the mixture of the solution was poured into the Petri dish and was dried in the fume hood for 24 hrs to produce the PMMA/TiO$_2$ nanocomposites in free standing form. The steps are illustrated in the figure 1 below. All the steps were repeated to prepare PMMA/TiO$_2$ nanocomposites with different weight percent of TiO$_2$. The amount of TiO$_2$ were varies from 1 to 20 wt%. The samples were then characterized using field emission scanning electron microscopy (FESEM), Raman spectroscopy and thermo gravimetric analysis (TGA). All the results will be discussed.

![Figure 1: Flow process for the preparation of PMMA/TiO$_2$ nanocomposites](image)

Sample Characterization
• FESEM
• Raman Spectroscopy
• TGA

Preparation of PMMA and TiO$_2$ solution

Sonication process

Mixing process

Solution casting process

Sonication process

Sample
Characterization
• FESEM
• Raman Spectroscopy
• TGA
3. Results and Discussions
The FESEM images show the surface morphology of nanocomposited PMMA/TiO$_2$ nanocomposites samples at different TiO$_2$ content. TiO$_2$ nanoparticles were found to be loaded into the PMMA phase, as indicated by the white regions that were shown in the figure 2(b-f). The different amounts of TiO$_2$ nanoparticles give the different morphology of the nanocomposites samples. Sample 0 w% TiO$_2$ nanofiller as shown in the figure 2(a) that contains only PMMA shows the porous structure with smooth film surface. In contrast, the surface morphology of the samples that contain TiO$_2$ nanoparticles are coarse and small crack were observed as shown in the figure 2(b-f). When TiO$_2$ nanoparticles were added into the PMMA, the porous structures disappear.

![Figure 2: FESEM images of nanocomposited PMMA/TiO$_2$ nanocomposites of (a) 0 wt% TiO$_2$, (b) 1 wt% TiO$_2$, (c) 5 wt% TiO$_2$, (d) 10 wt% TiO$_2$, (e) 15 wt% TiO$_2$ and (f) 20 wt% TiO$_2$.](image_url)

The different amounts of TiO$_2$ nanoparticles in the nanocomposites samples affect the structural properties of the nanocomposites samples where the cracks of the films morphology also increases as TiO$_2$ amount increase up to 10 wt% as shown in the figure 2(d). The dispersion of TiO$_2$ nanofiller in the polymer matrix plays important roles in identifying the final properties of the nanocomposites. Based on the previous study, the researcher reported that the good dispersion of TiO$_2$ filler in the PMMA will contribute to the increase in the glass transition temperature (Tg) value and also increase in mechanical properties of the nanocomposites samples [8]. In addition, other researchers found that the well dispersed of the metal oxides in the PMMA will improve its thermal stability and activation energy of the thermal degradation of the composites [9-12].

Further, Raman spectroscopy is used to study the phase content of the nanocomposited PMMA/TiO$_2$ nanocomposites. The TiO$_2$ nanoparticles are found to be encapsulated into the PMMA matrix. This can be seen in the figure 3(a-e), where the peaks of anatase were detected in the nanocomposites samples. The frequency of the Raman band for anatase TiO$_2$ peaks are identified at around: 147, 630, 513, and 519 cm$^{-1}$ [13]. Liu et al also reported that the peaks detected are same with the peaks detected in this study [14, 15].
Figure 3: Raman Spectrum of nanocomposited PMMA/TiO$_2$ nanocomposites of (a) 0 wt% TiO$_2$, (b) 1 wt% TiO$_2$, (c) 5 wt% TiO$_2$, (d) 10 wt% TiO$_2$, (e) 15 wt% TiO$_2$ and (f) 20 wt% TiO$_2$

Then, TGA is used to measure the thermal degradation of the nanocomposited PMMA/TiO$_2$ nanocomposites samples. The thermograms show the sample PMMA has low thermal degradation compared to the samples of nanocomposited PMMA/TiO$_2$ nanocomposites.

Figure 4: TGA analysis of nanocomposited PMMA/TiO$_2$ nanocomposites of (a) 0 wt% TiO$_2$, (b) 1 wt% TiO$_2$, (c) 5 wt% TiO$_2$, (d) 10 wt% TiO$_2$, (e) 15 wt% TiO$_2$ and (f) 20 wt% TiO$_2$

For the sample PMMA, the first stage of the thermal degradation occurs at around 120 °C which is same with the sample PMMA/TiO$_2$ nanocomposites. The second stage thermal degradation was observed at the temperature around 220 °C for the PMMA sample and the degradation temperature increase starts from about 240 °C for the PMMA/TiO$_2$ nanocomposites sample. The third stage observed at the temperature about 330 °C for the samples PMMA/TiO$_2$ nanocomposites and small stage observed for the sample PMMA. The thermal degradation temperature increases with the increase amount of TiO$_2$. From the thermograms, the degradation temperature that occurred below 150 °C can be attributed to the evaporation of incorporated water and decomposition of the peroxo groups that...
contain in the samples [15]. The degradation temperature that detected around 220 °C might be due to the decomposition of the small amount of head-to-head linkages in PMMA of unsaturated end groups of C=C bonds which are unstable [16, 17].

\[
\begin{align*}
\text{CH}_3 &\quad \text{CH}_2 \\
\text{CH}_2 - C - &\quad \text{CH}_2 - C - \\
\text{COOCH}_3 &\quad \text{COOCH}_3
\end{align*}
\quad \rightarrow \quad \text{CH}_2 - C - &\quad + &\quad \text{CH}_2 - C - \\
\text{COOCH}_3 &\quad \text{COOCH}_3 &\quad \text{COOCH}_3 &\quad \text{COOCH}_3
\]

(1)

The next degradation stage is initiated by the random C-C scission. It is predominant at higher temperature and occurs at about 300 °C. Some researcher reported that at around this temperature, the weak of head-to-head linkages of the main chain were ruptured. In addition, the decomposition temperature was detected at this temperature also might due to the terminal vinyl group decomposition [18, 19]. In the literature, Garzella et al reported that the most intense peak is observed at around this stage is due to depolymerization that initiated by the random chain scission [20].

Meanwhile, the activation energy observed is higher than the first reaction. At high temperature about 300 °C, the dominant mechanism occurred because it decompose PMMA into methyl methacrylate (MMA) as the major product as shown in the reaction 2 [17, 21-23].

\[
\begin{align*}
\text{CH}_3 &\quad \text{CH}_3 \\
\text{CH}_2 - C - &\quad \text{CH}_2 - C - \\
\text{COOCH}_3 &\quad \text{COOCH}_3
\end{align*}
\quad \rightarrow \quad \text{CH}_2 - C - &\quad + &\quad \text{CH}_2 - C - \\
\text{COOCH}_3 &\quad \text{COOCH}_3 &\quad \text{COOCH}_3 &\quad \text{COOCH}_3
\]

(2)

The intermediate products that further decompose produce the monomer. The reaction is shown below:

\[
\begin{align*}
\text{CH}_3 &\quad \text{CH}_3 \\
\text{CH}_2 - C - &\quad \text{CH}_2 - C - \\
\text{COOCH}_3 &\quad \text{COOCH}_3
\end{align*}
\quad \rightarrow \quad \text{CH}_2 - C - &\quad + &\quad \text{CH}_2 = C \\
\text{COOCH}_3 &\quad \text{COOCH}_3 &\quad \text{COOCH}_3 &\quad \text{COOCH}_3
\]

(3)

The degradation of the PMMA using TGA was done in the presence of oxygen. In the presence of oxygen, PMMA undergoes thermal oxidative decomposition due to the reaction of macro radicals with oxygen to form hydro peroxides which are unstable and will break down rapidly to give more free radicals. The main product of decomposition is monomer MMA. MMA will then further decomposed to produce smaller gaseous that are combustible. As described by previous studies, the monomer of MMA will break down to give small molecules by completing primarily two scission paths as shown in the equation below:
According to the authors, the equation 4 is the major reaction. Meanwhile equation 5 is the minor scission path [24].

From the thermograms, it is clearly indicates that the addition of the TiO$_2$ nanofiller in the PMMA shifted the degradation temperature to a higher temperature. The results are in accordance with the surface morphology that have been observed using FESEM where the researcher declared that the homogeneously distributed TiO$_2$ nanofiller in the PMMA matrix will slowing the thermal degradation of the nanocomposites and hence, lead to the increase in thermal properties of the nanocomposites compare to the sample that contain of only PMMA. All the samples PMMA/TiO$_2$ nanocomposites show the samples decomposed completely at about 400 °C, same with the sample PMMA. The amorphous structure of TiO$_2$ is converted to anatase phase as the temperature increases from 370 °C. The results were confirming with the Raman Spectroscopy results in the previous section. There is no weight loss on TGA curve after 400 °C for the PMMA/TiO$_2$ nanocomposites samples, indicates that the decomposition of TiO$_2$ precursor has complete and can start as a first annealing temperature.

The thermal stability observed is higher in the presence of TiO$_2$ filler. The reasons of this to occur is because of the basis restriction of mobility of the polymer chains which resulting from some factors such as the bonds which due to the adsorption of the polymer on the oxide surface via a methoxycarbonyl group, and also due to the steric hindrance which is due to the presence of the solid particles of the additives [25]. For the TiO$_2$ as filler, it can be assumed that the restriction of the mobility by oxide particles is also responsible for the increase of thermal stability, most likely by inhibiting a key step of the reaction mechanism involved that is key step occurring during the two first weight losses. The increase of the degradation temperature were generally considered as an indication of enhancement on the thermal stability of the PMMA/TiO$_2$ nanocomposites [26, 27].

4. Conclusion
The nanocomposited PMMA/TiO$_2$ nanocomposites were successfully produced using the sonication and solution casting method. From the results, it is found that the addition of nanosized TiO$_2$ filler can modify and increase the thermal properties of the nanocomposited samples. The samples that contain TiO$_2$ nanofiller have higher thermal degradation compared to the pure PMMA itself. The increase of the thermal degradation also reveals that the TiO$_2$ nanofiller was successfully dispersed in the PMMA as shown in the FESEM images where the successfully dispersed the filler in the polymer leads to increase in the thermal properties of the nanocomposites. Further studies have to be done on to study on the mechanical properties of these nanocomposited PMMA/TiO$_2$ nanocomposites samples.

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