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Impact and Fire Resistance Properties of Polypropylene Filled with Graphene/$Mg(OH)_2$ nanoparticles

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Abstract:

Nanocomposites made from graphene nanoplatelets (GN) and magnesium hydroxide (Mg(OH)2) based on polypropylene (PP) matrix were prepared via melt-mixing in an internal mixer, and followed by compression molding. The composition ratios of GN/Mg(OH)2 were varied by the GN from 0.5 to 1.5 wt.% and Mg(OH)2 from 5 to 15 wt.%. The impact mechanical property and fire resistance of PP nanocomposites were examined. The significance effects of GN and Mg(OH)2 loadings were determined via statistical analysis. The solely inclusion of GN had increased the impact strength and fire resistance of PP with the maximum level achieved at 1 wt.% GN. By adding Mg(OH)2 into GN filled PP nanocomposites, it showed a reduction in impact strength with the increase of fillers loading, whilst for fire resistance, the burning rates were the lowest at the composition ratios of 0.5/10 wt.% GN/Mg(OH)2 and 1/5 wt.% GN/Mg(OH)2. Statistical analysis proved the significant individual effect of GN and Mg(OH)2 loadings on both properties but insignificant interaction between both parameters (loadings of GN and Mg(OH)2). In the presence of Mg(OH)2, scanning electron microscope (SEM) micrograph showed a more porous microstructure of nanocomposites.

***Keywords:** Nanocomposite, fire retardant, ANOVA, morphology*

I. INTRODUCTION

Polypropylene (PP) is a crystalline polyolefin, which has some good characteristics including low cost, lightweight, highly recyclable, ease of processing, and superior properties such as high toughness and corrosion resistance. However, there are a few shortcomings for PP like extremely high flammability and poor thermal conductivity, as compared to other polymers [1, 2]. The fire resistance behavior of polymer matrix composites has been attracted researchers' attention for investigation because fire resistance is a serious safety matter, which is necessary in industrial safety applications [3]. Magnesium hydroxide, $Mg(OH)_2$, is a kind of fire-retardants which is versatile and commonly applied to reduce polymer flammability. $Mg(OH)_2$ is one of the fire retardants which is suitable be used in polymers such as PP because of its decomposition to generate byproducts of magnesium oxide (MgO) and water beginning from 300–320 °C (before the decomposition of polymers, i.e. ~450 °C for PP) [4, 5]. However, the high concentration of $Mg(OH)_2$ may deteriorate the mechanical performance of the final composite material [6].

Graphene nanoplatelets (GN) are multi-layers graphite nanocrystals in the form of platelets, which possessing superior thermal stability, mechanical and electrical properties. Graphene filled polymer nanocomposites have acted as potential candidate in various applications such as green technology, automobile, aerospace, electronic and defense industries [7]. In the past researches, it was reported that the properties of a polymer could be enhanced remarkably with the incorporation of only a small concentration of GN. For instances, the performance improvements of Charpy impact fracture strength by 0.3- 0.4 wt.% GN [8], tensile and thermal stability properties by 0.1-0.5 wt.% GN [1, 5], electrical

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conductivity (percolation phenomenon shown) by 5 wt.% GN [9], and etc.

The use of two or more reinforcements, so called hybrid composite, is one of the strategies to improve the nanocomposite performance by counterbalancing some of the weaknesses of a particular filler [10]. Guan et al. stated that hybrid fillers with different dimensions could expedite a dense and efficient heat transfer networking, and cause to a subsequent improvement in thermal conductivity property [11]. To the best of our knowledge, the effect of GN/$Mg(OH)_2$ composition ratio on thermoplastic has not been investigated yet. In this paper, the influence of GN and $Mg(OH)_2$ loadings, and their synergistic effects on the impact strength and fire resistance properties were studied. The significance effect on the properties was discussed with aid of statistical analysis.

II. EXPERIMENTAL PROCEDURES

Polypropylene (PP), graphene nanoplatelets (GN) and/or without magnesium hydroxide ($Mg(OH)_2$) were melt-compunded using an internal mixer (Thermo Haake Rheomix 600P). The mixing process parameter was set at 180 °C, 100 rpm and 13 min. The neat PP sample acted as the control sample. Two experimental variables in this study were the loadings of GN and $Mg(OH)_2$, which were varied at 0.5-1.5 and 5-15 wt.%, respectively. Maleic anhydride-grafted-polypropylene (MA-g-PP) was incorporated into the nanocomposites by half of the GN loading. The blended compounds were then undergone compression molding in a compression machine (LP50, LABTECH Engineering Company) at 180 °C and for 16 min.

Impact property of the specimens was determined using a Ray-Ran Universal Pendulum Impact System in accordance with ASTM D256-05 under a load of 0.452 kg. The velocity of 3.46 ms^{-1} and calibration energy of 2.765 J were applied. Burning testing (ASTM D5048-90) was carried out to investigate the fire resistance by determining the rate of burning, which was the burned length (cm) divided by the burning process period (min). Two-factor analysis of variance (ANOVA) was used to perform the statistical significance (5% significance level) effect of GN and $Mg(OH)_2$ loadings on the experimental impact and fire resistance results, with aid of Data Analysis ToolPak in Excel. The morphology of fractured surface was observed using variable-pressure scanning electron microscopy (Philips XL 30).

III. RESULTS AND DISCUSSION

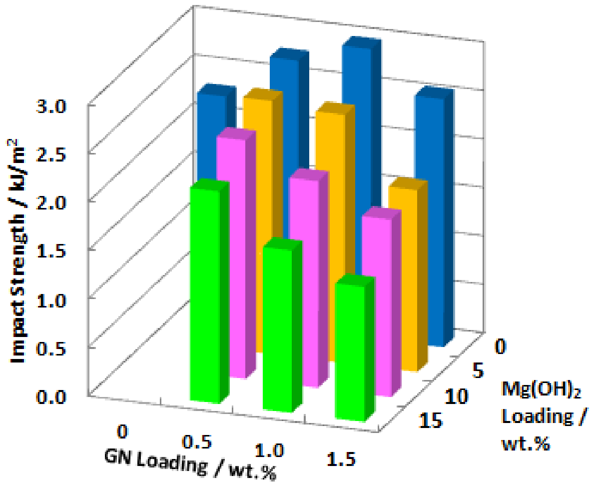

Fig. 1. Effect of GN and $Mg(OH)_2$ loadings on the impact strength of PP nanocomposites.

Figure 1 displays the influence of GN and $Mg(OH)_2$ loadings on the impact strength of PP nanocomposites. The neat PP (without GN and $Mg(OH)_2$) exhibited the impact strength of 2.3 kJ/m^2. The inclusion of GN alone into PP nanocomposites at a low loading has resulted in the improvement of impact strength, as indicated by the last row (blue bars) in Figure 1. The maximum impact strength achieved at 1.0 wt.% GN which recorded ~ 3 kJ/m^2, and the decrement was seen after the optimum loading of 1.0 wt.% GN. This trend is similarly reported by Liang (2019) who studied PP composites with different types of GN and averagely 0.3-0.4 wt.% GN was found to attain the highest impact strength [8]. The latter decrease in impact strength of PP/GN nanocomposites is due to the increase of rigidity characteristic imparted by the high loading of GN [12]. For hybrid nanocomposites, the inclusion of $Mg(OH)_2$ into PP/GN nanocomposites gave a negative effect on the impact strength. As the $Mg(OH)_2$ loading increased, the impact strength of PP/GN nanocomposites reduced gradually, irrespective of GN loading. The reduction in impact strength is expected and this trend is commonly reported for the composites material containing fire retardants because fire retardant ($Mg(OH)_2$ in this study) is a rigid material. The distribution energy of rigid fire retardants contributed the impact resistance reduction [13].

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The burning rates of the PP nanocomposites are shown in Figure 2, which are ranged from 4.5 cm/min to 7.7 cm/min. The neat PP had the highest rate of burning, which indicates the ease-flammable property of polymer. With the addition of GN and $Mg(OH)_2$, the burning rates of nanocomposites were much lower than that of PP. This implies the significant improvement of flame retardancy of PP nanocomposites. The composites reinforced with single GN nanofillers exhibited the reduced material flammability as a result of the formation of a dense barricading graphitized char-layer which restricting the mass-loss [14]. Meanwhile, the inclusion of $Mg(OH)_2$ particles into PP/GN nanocomposites resulted in a synergic effect on burning rates. This reduction may be elucidated by the physical character of $Mg(OH)_2$, including (1) its endothermic nature that required high thermal input to complete the combustion process, (2) the decomposition byproduct (water) to dilute the flammable volatiles, and (3) a layered material is formed on the composite surface to prevent the passage of oxygen [15].

The deviation of impact strength and fire resistance is demonstrated in Figure 3. As compared to neat PP, the impact strengths were positively and negatively affected by each GN and $Mg(OH)_2$ presence, as observed in Figure 3 (a). In the nanocomposites with higher loading of GN, the higher the $Mg(OH)_2$ loading, the more the deterioration of impact strength, which reduced up to 40% for PP nanocomposite reinforced hybrid fillers of 1.5 wt.% GN/15 wt.% $Mg(OH)_2$. However, the incorporation of GN/$Mg(OH)_2$ fillers, irrespective of the composition ratio, led to the improvement in fire resistance by 20-40 %. The highest fire resistance enhancement was achieved for nanocomposites containing GN/$Mg(OH)_2$ at the composition ratio of 0.5/ 10 (wt.%). The ANOVA results (Table 1) proved the statistically significant effects of both GN and $Mg(OH)_2$ loadings on the impact strength but insignificant effect on the fire resistance properties. For individual effects of GN and $Mg(OH)_2$ loading on the impact strength, the P-values are less than the significant level (0.5) and the F-values are greater than F-critical. Nevertheless, the significant interaction between GN and $Mg(OH)_2$ loadings is only shown for burning rate.

Figure 4 shows the SEM micrographs of (a) PP/GN and (b) PP/GN/$Mg(OH)_2$. The PP/GN nanocomposite system in Figure 4 (a) showed a tighter texture in comparison to the PP/GN/$Mg(OH)_2$ nanocomposite system. The more porous structure in the sample in Figure 4 (b) could explain the decrease in the impact mechanical strength of nanocomposite material containing fire retardant [13].

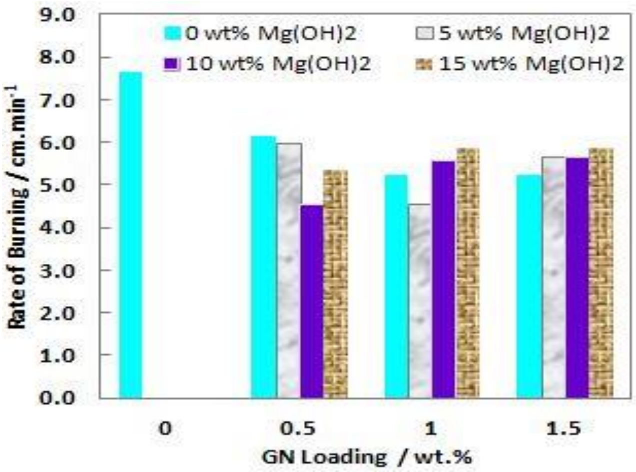

Fig. 2. Effect of GNP and $Mg(OH)_2$ loadings on the burning rate of PP nanocomposites.

Figure 1. Surface morphology of synthesized TiO_2-Cu_2O-CuO/Cu(a) and ZnO-Cu_2O-CuO/Cu (b) after thermal oxidation at x60K magnification

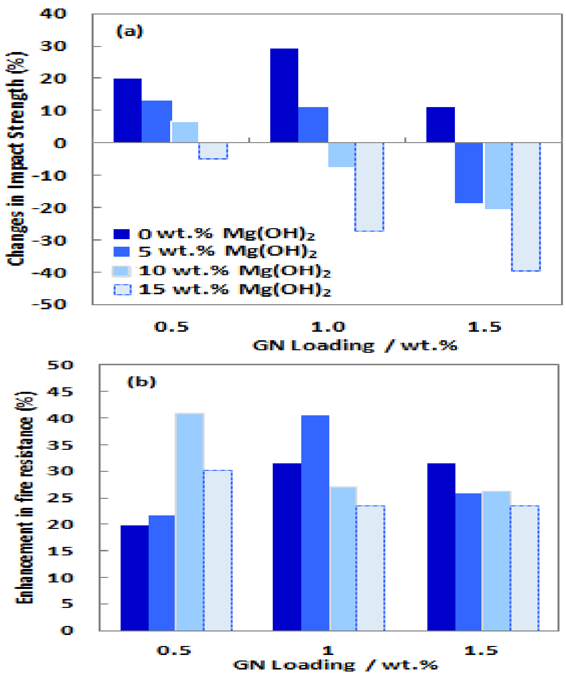

Fig. 3. Deviation of impact strength and fire resistance in PP nanocomposites. Note: the deviation is calculated based on neat PP (control sample).

Table 1. Two-factor ANOVA test on the influence of GNP loading and $Mg(OH)_2$ loading on impact strength and rate of burning

Variables	Source of	Impact	Rate of

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	Variation	Strength	Burning
GNP loading	P-value	7.46E-07	0.322
	F-value	26.89	1.25
	F-critical	3.40	3.89
$Mg(OH)_2$ loading	P-value	2.25E-09	0.280
	F-value	38.90	1.44
	F-critical	3.01	3.49
GNP loading × $Mg(OH)_2$ loading	P-value	0.054	0.005
	F-value	2.46	5.71
	F-critical	2.51	3.00

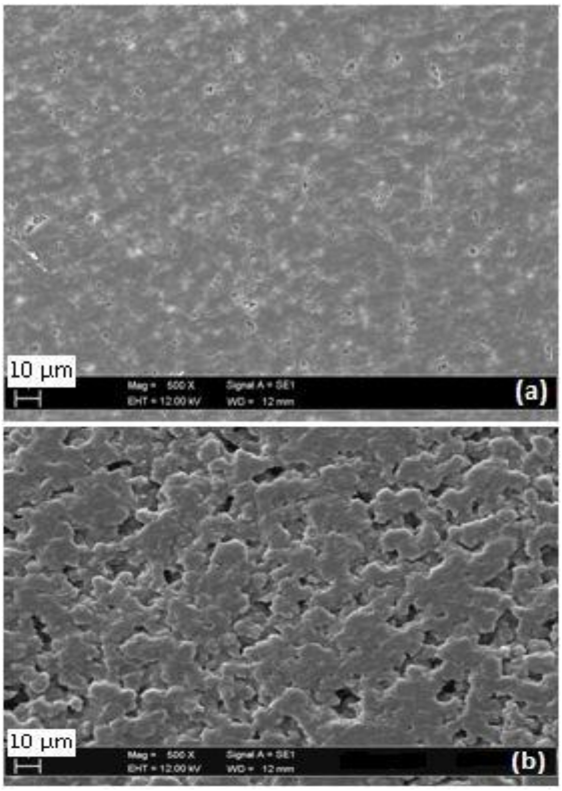

Fig. 4. SEM micrograph of PP nanocomposites containing (a) GN and (b) GN/$Mg(OH)_2$.

IV. CONCLUSION

In summary, the PP/GN and PP/GN/$Mg(OH)_2$ nanocomposites were successfully fabricated through melt-blending method. The effects of GN and $Mg(OH)_2$ on the composites impact strength and burning rate were studied. The incorporation of hybrid fillers at the composition of 1 wt.% GN and 5 wt.% $Mg(OH)_2$ promoted the synergistic effect in impact and fire-retardancy improvements.

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Ruey Shan Chen is currently a senior lecturer in Materials Science Program, Faculty of Science and Technology, Universiti Kebangsaan Malaysia (UKM). She obtained her first degree and doctor of philosophy degree in Materials Science from UKM. She has published in polymers and bio-, nano- and hybrid composites field. The common journals she published are Journal of Applied Polymer Science, Polymer Composites, Composites Part B, BioResources and other related journals. The recent google scholar h-index and i10-index are 11 and 12, respectively. Her research interests are on the fabrication of composites, biocomposites and nanocomposites made from recycled polymer, blends, agricultural wastes or/and multifunctional nanoparticles. For examples, she had developed a high loading (of rice husk) biocomposites based on recycled polyolefin blends. In recent year, her research area expands to lightweight porous/circular composite materials. I am a member of Polymer Research Center (PORCE).

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