Effect of Oil Palm Ash on the Properties of Polypropylene/Recycled Natural Rubber Gloves/Oil Palm Ash Composites

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In the present study, polypropylene, recycled natural rubber gloves, and oil palm ash composites (PP/rNRg/OPA) were prepared using an internal mixer. The effects that OPA loading had on the processability, tensile properties, morphology, and thermal stability of the PP/rNRg/OPA composites were investigated. The stabilization torque, tensile modulus, and thermal stability all increased; however, the elongation at break decreased as the OPA loading increased. The tensile strength increased to a maximum of 4 parts per hundred rubber (phr) OPA loading, and subsequently decreased. At 4 phr OPA, the filler was well-dispersed and had a good interaction with the matrix, whereas the agglomeration and detachment of OPA was observed at high loading rates of OPA in the PP/rNRg/OPA composite. Thermogravimetric analysis (TGA) indicated that the thermal stability of the composite increased as the OPA loading increased. Further evidence for the increased thermal stability can be found when analyzing the decomposition temperatures at different stages and maximum weight loss, where higher decomposition temperatures corresponded to composites with higher OPA loadings.

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INTRODUCTION

Composites are typically produced using relatively expensive raw materials. Expenses, coupled with the increased awareness of the environmental problems incurred within the industry, have caused people to consider the notion of using alternative materials in composites. One potential component that has gained recent attention is ash, a by-product of combustion activities. Numerous studies have been conducted using ash as a filler in polymer composite, including studies of fly ash (Ahmad and Mahanwar 2010), plerospheres (Wang *et al.* 2004), rice husk ash (Ismail *et al.* 1999; Sereda *et al.* 2003), volcanic ash (Trinidad *et al.* 2010), coir dust (Mishra and Aireddy 2011), and oil palm ash (Bhat and Abdul Khalil 2011; Khalil *et al.* 2012; Ooi *et al.* 2013).

In Malaysia, the production and exportation of palm oil has been growing rapidly, subsequently leading annually to millions of tonnes of oil palm waste. The solid waste from palm oil production can be turned into an alternative fuel for steam generation in palm oil plants, which in turn produces the by-product known as oil palm ash (OPA). Foo and Hameed (2009) reported that 4 million tonnes of OPA is produced annually, which is predicted to increase with increasing demand for palm oil. After the combustion process, the OPA is normally dumped in a landfill or a field, causing environmental problems

(Foo and Hameed 2009; Ismail and Shaari 2010). To solve this problem, oil palm ash should be utilized and turned into a valuable product.

Abundance of waste rubber has created huge environmental problems due to its non-degradable character. General methods of disposing waste rubber are landfilling, pyrolysis, and incineration, each of which causes environmental pollution (Hall *et al.* 2009; Nabil *et al.* 2013). Considering the environmental and economic advantages, recycling is one of the best options. A number of possible applications of various forms of waste rubber in broad disciplines have been studied and reported (Ismail *et al.* 2009; Ragunathan *et al.* 2014; Ling and Ismail 2013). Therefore, we have used a recycled NR gloves (obtained from industrial production rejects) in an effort to create valuable materials. Reutilization of waste rubber can be achieved by mechanical and chemical processing. However, the reutilization of waste rubber by mechanical processing has the potential to be more cost-effective compared to chemical processes.

In recent years the incorporation of filler in recycled rubber containing thermoplastic elastomers has received much attention. The addition of fillers has a high impact upon economics for thermoplastics, while a general improvement in certain properties is also achieved. For example, the addition of rice husk in PP/recycled NBR was previously studied by Ragunathan *et al.* (2012). It was observed that the balance set of tensile strength and elongation at break of the composites was still achievable at the loading up to 10 phr of the rice husk in the composites. More recently, a study on the incorporation of kenaf fiber filled polypropylene/waste pulverized tire was reported by Ling and Ismail (2013). It was also found that the acceptable properties were gained upon the addition of kenaf fiber in the polymer matrix.

From this point of view, turning the waste materials into potential composites has received increasing attention. To date, no attempts have been made to use OPA in combination with new blending materials, namely polypropylene/recycled natural rubber gloves (PP/rNRg) composites. Therefore, in order to develop new composite material, the objective of this work is to study the effect of OPA loading on the processability, tensile properties, thermal stability, and morphology of an OPA-filled polypropylene/recycled natural rubber glove (PP/rNRg/OPA) composite.

EXPERIMENTAL

Materials

The polypropylene (PP) used in this work was PP Grade 6331, supplied by Titan Pro Polymers (M) Sdn. Bhd. (Johor, Malaysia). The polypropylene has a melting point of 160 ^{o}C, a melt flow index of 14 g/10 min at 230 °C, and a density of 0.9 g/cm^3. The recycled natural rubber gloves (rNRg) have a density of 1.015 g/cm^3 and were supplied by Juara One Resources Sdn. Bhd. (Penang, Malaysia). The rNRg were first pre-ground by passing through a two-roll mill at room temperature, then ground into a powder (sizes ranging from 117 to 334 μm) using a Table Type Pulverizing Machine from Rong Tsong Precision Technology Co., Ltd. (Taiwan).

Oil palm ash was obtained from the United Oil Palm Mill (Penang, Malaysia). The main elemental composition (wt%) of the OPA, as analyzed with a Rigaku RIX3000 X-ray fluorescence (XRF) spectrometer (Japan), was as follows: C (41.5), SiO_2 (34.0), CaO (7.3), Al_2O_3 (3.9), MgO (3.8), K_2O (3.7), P_2O_5 (3.2), Fe_2O_3 (1.9), and trace elements (0.7). The OPA was dried in a vacuum oven at 80 °C for 24 h to expel any remaining

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moisture, then ground with a ball mill to powder form and sieved. Figure 1 shows an SEM micrograph of the OPA after the grinding process. The OPA particles were irregular in size and shape, suggesting that the addition of OPA to PP/rNRg/OPA can increase the reinforcement of the composite. It was also observed that the OPA particle sizes ranged from 10 to 40 μm, *i.e.*, fine particles that can be applied as filler for PP/rNRg/OPA composites.

Methods
Preparation of the composites

The formulation of CB filled PP/rNRg composites are presented in Table 1. All the materials were melt-mixed with an internal mixer (HAAKE Rheomix Mixer Model R600/610, Germany) at 180 °C, with a rotor speed set at 50 rpm. The weight ratio of PP to rNRg was fixed at 70/30 (parts per hundred (phr)/phr). The PP pellets were added gradually into the hopper, and the rNRg was added after 4 min of mixing. The mixing was continued for another 2 min, after which the OPA was added at 0, 2, 4, 6, or 10 phr and left to melt for 3 min. The total mixing time was 9 min. The torque changes upon the processing time and the stabilization torque were recorded. Finally, the PP/rNRg/OPA composites were compression-molded in a KT-7014 A electrically heated hydraulic press (GoTech Testing Machines Inc., Taiwan) to produce molded sheets of composites. The compounded sample was first preheated for 6 min, followed by compression for 4 min at a temperature of 180 °C. The sample was then cooled under pressure for 2 min at ambient temperature.
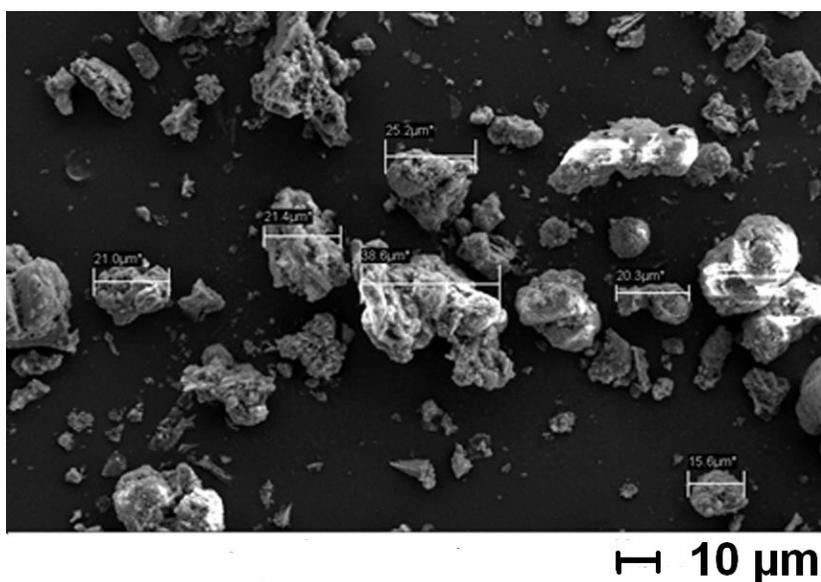

Fig. 1. SEM micrographs of oil palm ash

Table 1. Formulation of OPA filled P/rNRg Composite

Materials	Composition (phr)
Polypropylene (PP)	70
Recycled natural rubber gloves (rNRg)	30
Oil palm ash (OPA)	0, 2, 4, 6, 10

Measurement of tensile properties

The molded composite sheets were cut into dumbbell-shaped specimens using a Wallace die cutter (United Kingdom). The tensile test of the sheets was performed at a cross-head speed of 5 mm/min with a constant gauge length of 50 mm using a Universal Tensile Machine (Instron 3366, USA), in accordance with ASTM D412-06a (2013). The tests were performed at 25 ± 3 °C on 1 mm-thick composite sheets. The average of five readings of tensile strength, tensile modulus, and elongation at break were recorded.

Scanning electron microscopy

The examination of OPA and the tensile fractured surfaces were carried out using a Leo Supra-35VP Field Emission Scanning Electron Microscope (SEM) operating at an accelerating voltage of 10 kV. The OPA and fractured pieces were mounted on aluminum stubs and sputter coated with a layer of gold/palladium to eliminate electrostatic charge during examination.

Thermogravimetric analysis

Thermogravimetric analysis (TGA) was performed using a Perkin-Elmer Pyris 6 TGA analyzer (USA), at temperatures ranging from 30 to 600 °C, with a heating rate of 10 °C/min, under a nitrogen flow of 20 mL/min.

RESULTS AND DISCUSSION

Processing Properties of PP/rNRg/OPA Composites

The torque development of PP/rNRg/OPA composites is shown in Fig. 2. At the beginning of the mixing process, the torque initially increased when the pure PP was added to the internal mixer through the hopper. This increment was due to rigid pellet-form of the PP which has not melted at the beginning of the feeding step, thus causing resistance to flow and resulting in a high torque value. The torque later decreased after 1 min of mixing because the pellets softened.
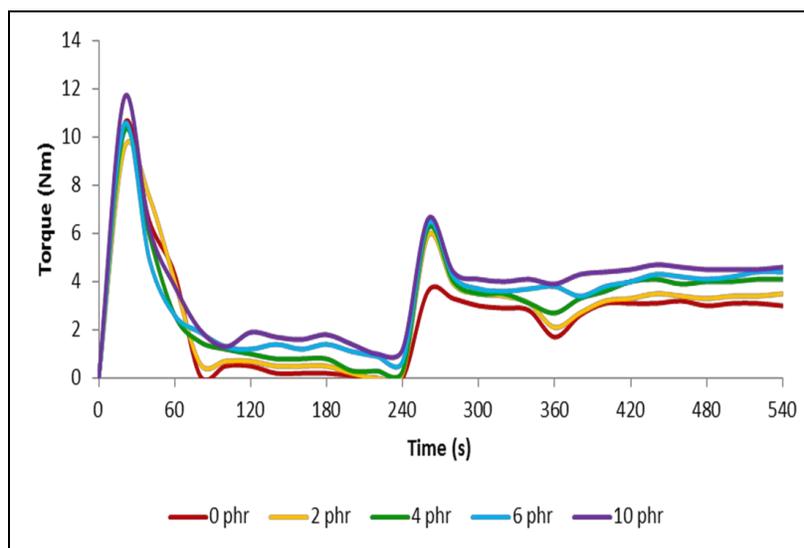
Fig. 2. Torque development of PP/rNRg/OPA composites at various OPA loadings

After 4 min, the torque increased again because of the incorporation of the rNRg particles. The viscosity of the composite increased, and therefore higher force was needed for the purpose of shearing and mixing. After 6 min, the torque increased yet again with the addition of OPA. Finally, the torque decreased and stabilized until the 9th minute (Fig. 3). The stabilization torque increased with OPA content because higher shear force was needed to incorporate the OPA into the PP/rNRg matrix to achieve proper mixing.
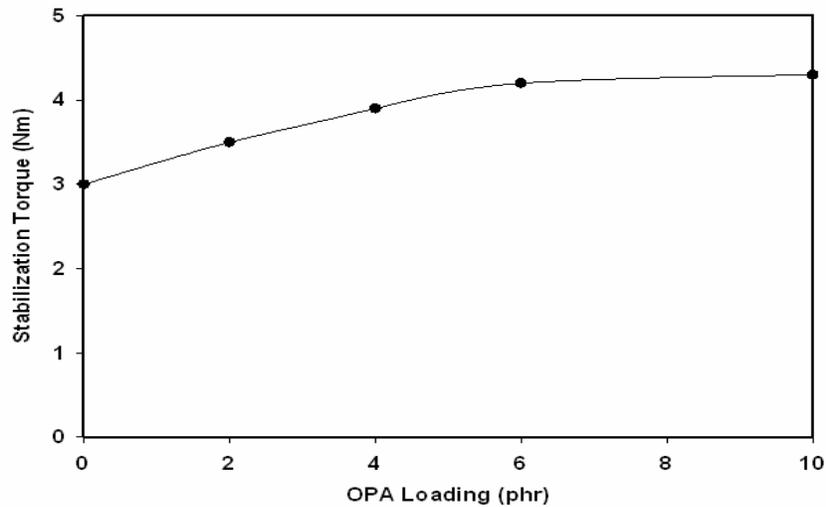

Fig. 3. Stabilization torque (at the 9th minute) of PP/rNRg/OPA composites at various OPA loadings

Tensile Properties of PP/rNRg/OPA Composites

The tensile strengths of the OPA-filled polypropylene/recycled natural rubber glove (PP/rNRg) composites are presented in Fig. 4. The tensile strength of PP/rNRg/OPA composites increased as the OPA loading increased, up to 4 phr, after which it subsequently decreased.
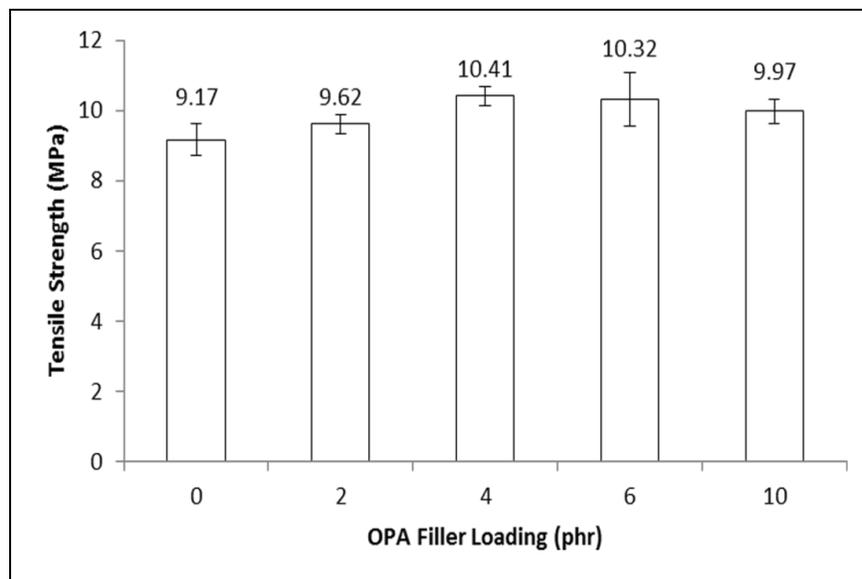

Fig. 4. Tensile strength of PP/rNRg/OPA composites at various OPA loadings. Data presented as the average ± standard deviation

The tensile strength of composites filled with 4 phr OPA was 13.5% higher than that of the unfilled composite. Further addition of OPA loading (beyond 4 phr) decreased the tensile strength of the composite. Although the tensile strength of the composite decreased, the tensile strength of the composite with 10 phr OPA was still 8.7% higher than that of the unfilled composite.

It is believed that the OPA particles can become fully saturated by the PP/rNRg matrix, especially at low OPA loadings. The polymer chain can penetrate the pores of OPA and become part of the filler. In addition, the well-dispersed and embedded OPA in the matrix promoted better tensile strength. However, at higher OPA loading, particularly at OPA loading rates beyond 4 phr, the filler particles tended to agglomerate, thereafter being less wetted and less penetrated by the polymer chains, which had a detrimental effect on the tensile strength. Also, at high OPA loadings, the filler failed to support the stress transferred from the polymer matrix because of the agglomeration of OPA.

Figure 5 shows that the elongation at break decreased as the OPA filler loading increased. The elongation at break was 4.61% for unfilled composites; however, that value dropped to 3.33% for the PP/rNRg/OPA composite with 10 phr OPA. Consequently, the overall decrease in elongation at break is 27.8%. Furthermore, the OPA can improve the stiffness of the composites. The OPA embedded in the matrix restricted the freedom of the polymer chains and reduced the flexibility of the composites as well.

Figure 6 shows the tensile modulus of PP/rNRg/OPA composites. The modulus increased as the OPA loading increased. The modulus of the unfilled composite was 440.90 MPa, increasing up to 644.97 MPa for the composite with 10 phr OPA filler loading. The overall increment was 46.3%. The addition of OPA has been found to cause a reduction in chain mobility while also increasing the rigidity of composites (Ismail *et al.* 2009).
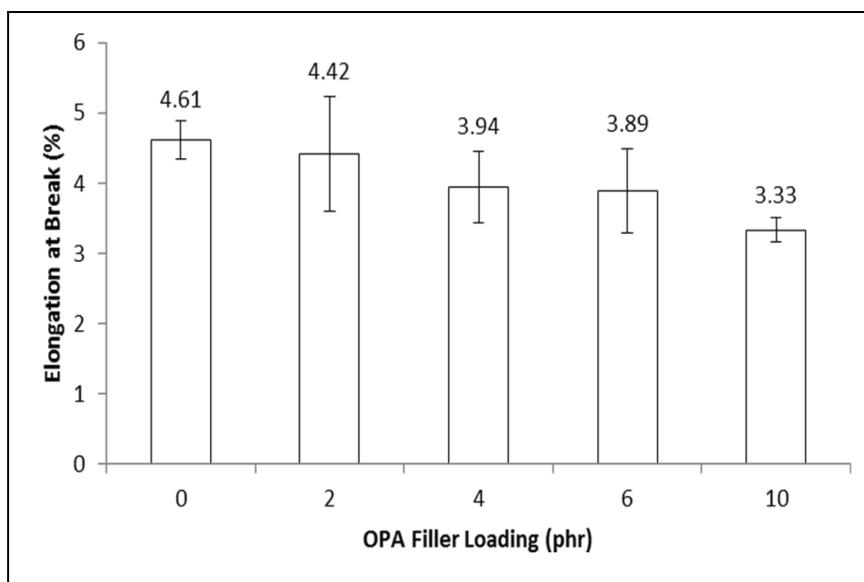

Fig. 5. Elongation at break of PP/rNRg/OPA composites at various OPA loadings. Data presented as the average ± standard deviation
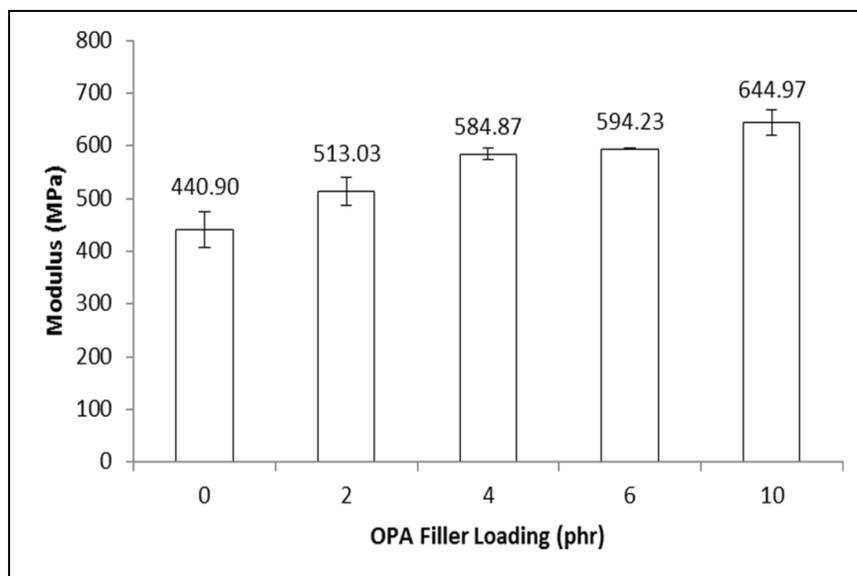
Fig. 6. Tensile modulus of PP/rNRg/OPA composites at various OPA loadings. Data presented as the average ± standard deviation

Tensile Fractured Surfaces

The morphology of an unfilled PP/rNRg composite is shown in Fig. 7. It is apparent that the rNRg was well-embedded in the PP matrix due to good interaction between the rNRg and PP. Figure 8 shows the tensile fractured surface of a PP/rNRg/OPA composite filled with 4 phr OPA. It can be seen that the OPA was embedded strongly in the PP matrix, exhibited by the fact that there was no gap around the OPA. Moreover, the fractured surface showed no sign of filler agglomeration or filler pull-out from the matrix. Good adhesion between the filler and polymer matrix leads to better stress transfer across the interface. The OPA can support the stress transferred from the matrix, which leads to better tensile strength of PP/rNRg/OPA composites.
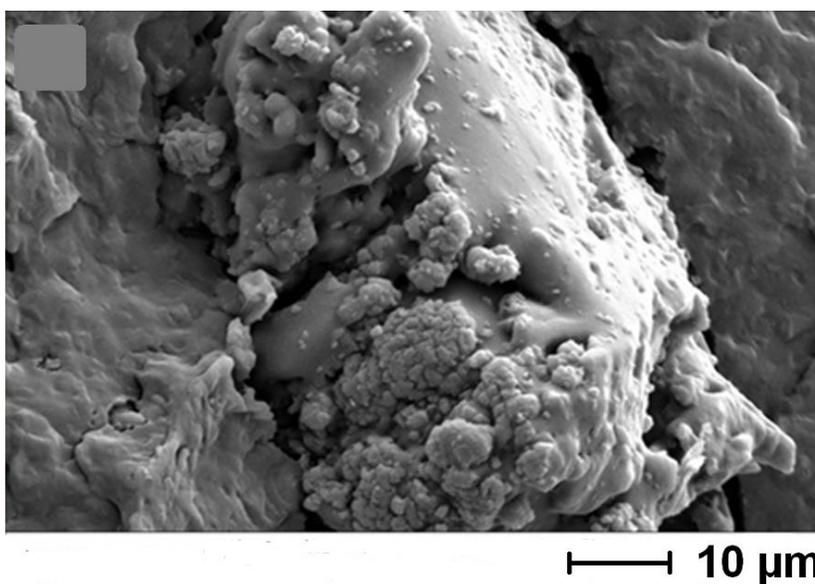

Fig. 7. SEM micrographs showing morphology of PP/rNRg composite without OPA loading
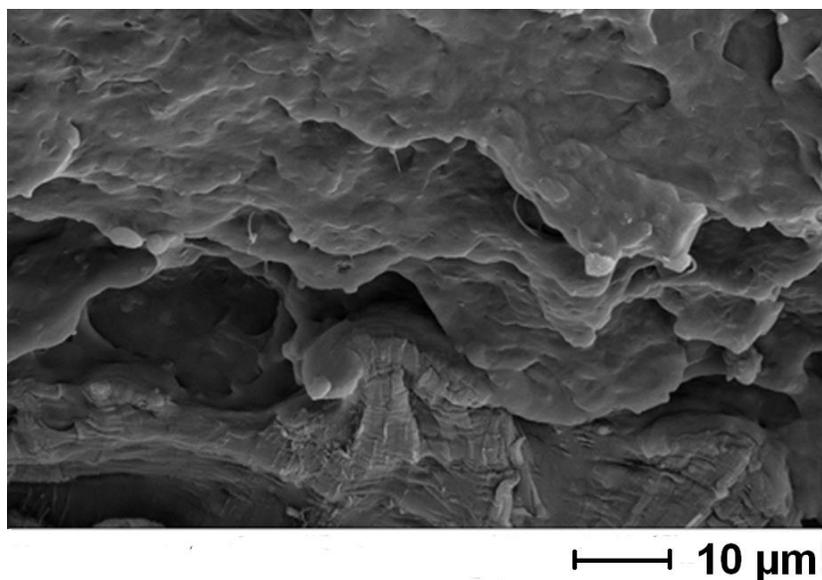
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Fig. 8. SEM micrographs showing morphology of PP/rNRg/OPA composite filled with 4 phr OPA

Figure 9 shows the morphology of the tensile fractured surface of PP/rNRg/OPA filled with 10 phr OPA. Figure 9a shows the agglomeration of OPA, whereas Fig. 9b shows the detachment of OPA, which causes the formation of voids or gaps on the fractured surface of the PP/rNRg/OPA composite. The filler particles were detached due to weak bonding between the particles and the matrix interface in the composite (Kraus *et al.* 1997; Kader *et al.* 2006). The detachment of the OPA from the matrix demonstrated the poor wettability of OPA by PP/rNRg matrix at high filler loading.
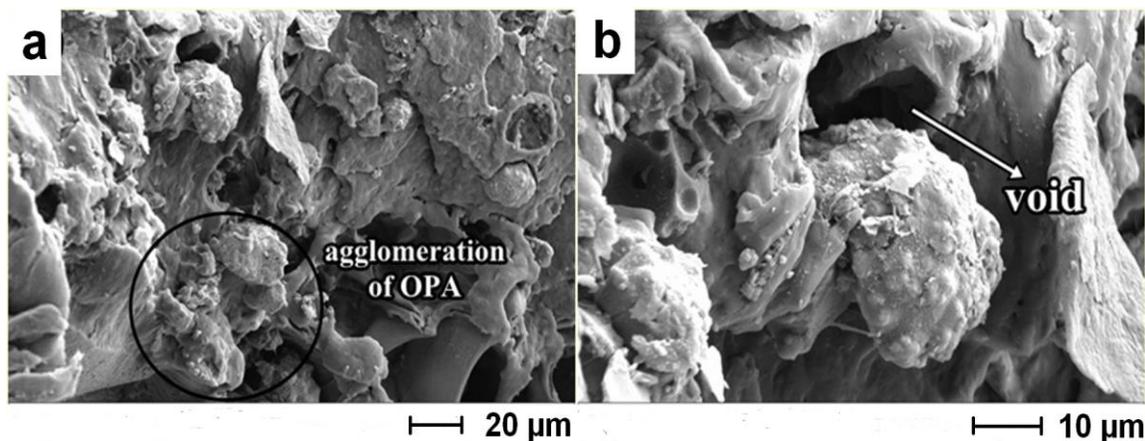

Fig. 9. SEM micrographs showing the fractured surface of PP/rNRg/OPA composite filled with 10 phr OPA: (a) the agglomeration of OPA in PP matrix at 500× magnification; (b) the OPA is pulled out from the matrix.

Thermogravimetric Analysis of PP/rNRg/OPA Composites

Figure 10 shows the typical TGA weight loss curve for the various OPA loadings for PP/rNRg/OPA composites; the summarized output obtained from the TG profile is given in Table 2. It can be seen that the curve tended to shift to a higher decomposition temperature when the OPA loading was increased. The unfilled composite started to show thermal degradation (5% weight loss) at 332.83 °C, and 100% weight loss at 583

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°C. For 50% weight loss, the unfilled composite became degraded at 444.60 °C. The PP/rNRg/OPA composite filled with 2 phr OPA started to degrade (5% weight loss) at 368 °C, and later sustained 50% weight loss at 459.68 °C. The composite shows a 10.6% and 3.4% improvement in the thermal stabilities of T_5 and T_{50}, respectively, after the addition of 2 phr OPA into the composite. With further addition of OPA filler into the composite, the T_5 and T_{50} of the PP/rNRg/OPA composite at 4 and 10 phr OPA were 389.62 °C/468.96 °C and 392.86 °C/470.87 °C, respectively. Furthermore, the increment of thermal stability in terms of T_5 and T_{50} for the PP/rNRg/OPA composites at 4 phr OPA was 6% and 2%, respectively, whereas the 10 phr OPA loading in the composites showed 0.83% and 0.4% of improvement in T_5 and T_{50}, when compared to composites with 4 phr OPA loading. Overall, the filled composites with 10 phr of OPA showed an 18% and 5.9% improvement of thermal stability regarding T_5 and T_{50} when compared to unfilled composites.
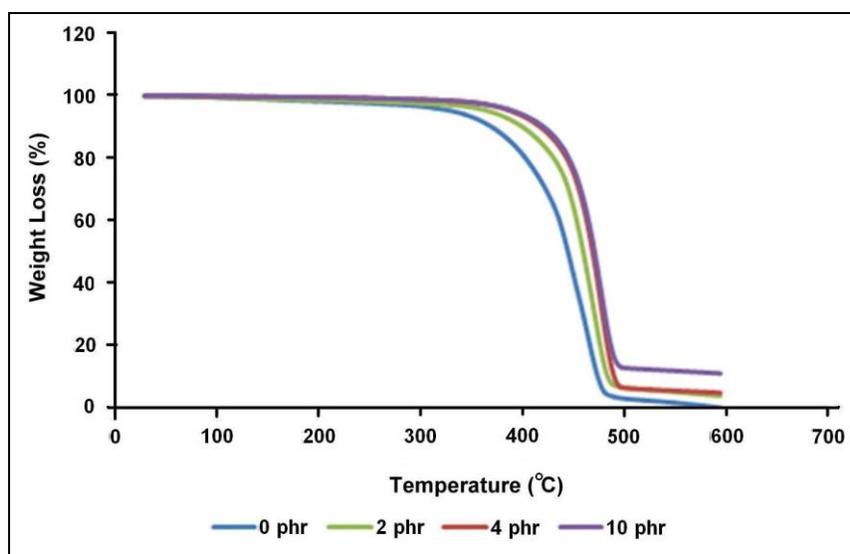

Fig. 10. TG curves of PP/rNRg/OPA composites filled with different OPA loadings

Table 2. Decomposition Temperatures at 5%, 50%, and Maximum Weight Loss and Char Residue for PP/rNRG/OPA Composites

Samples	T_5 (°C)	T_{50} (°C)	T_{max} (°C)	Amount of residue left (%)
PP/rNRg	332.83	444.60	465.06	0
PP/rNRg/OPA 2 phr	367.99	459.68	471.48	3.68
PP/rNRg/OPA 4 phr	389.62	468.96	476.89	4.60
PP/rNRg/OPA 10 phr	392.86	470.87	477.55	10.84

Furthermore, the amount of residue remaining (taken at 590 °C) increased as the OPA loading increased in the composite. This clearly indicates that the OPA was not burnt off at temperatures below 600 °C due to the inert atmosphere and the combination of inorganic materials that remained in the raw OPA. The maximum degradation temperatures of PP/rNRg/OPA composites filled with various OPA loadings are summarized in Table 2. The maximum degradation temperature, T_{max}, is represented by the peak temperature, which indicates the maximum degradation rate of the composite. It was found that the maximum degradation temperature for a given unfilled composite was

465.06 °C, which increased slightly to 471.48, 476.89, and 477.55 °C for composites filled with 2, 4, and 10 phr OPA, respectively. This suggests that higher temperatures are required to break the network chain, which was supported by the incorporation of OPA. Well-dispersed and embedded OPA in the composites are clearly responsible for the improvement of the thermal stability for PP/rNRg/OPA composites. It is generally believed that the inclusion of inorganic components into organic materials can improve the thermal stability of the composite (Ooi *et al.* 2013). The dispersion of OPA can hinder the diffusion of volatile decomposition products in the composite matrix, such that a higher temperature is required to decompose the PP/rNRg/OPA composites.

CONCLUSIONS

1. The stabilization torque and tensile modulus increased as the OPA loading increased; whereas the tensile strength of the PP/rNRg/OPA composites increased up to 4 phr OPA and then decreased with further addition of OPA. On the other hand, the elongation at break decreased as the OPA loading increased.

2. The SEM micrographs of the PP/rNRg/OPA composites filled with 4 phr OPA showed good interfacial interaction and filler-polymer interaction with the addition of OPA.

3. The incorporation of OPA also increased the thermal stability of PP/rNRg/OPA composites, which can be attributed to the shifting of the decomposition temperatures to a higher region.

4. Well-dispersed and embedded OPA in the composites are clearly responsible for the improvement of the overall properties of the PP/rNRg/OPA composites.

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