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Comparison of the Effects of Palm Oil Ash, Carbon Black and Halloysite Nanotubes on the Properties of Polypropylene/Recycled Natural Rubber Glove Composites

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Abstract: *The comparative effects of palm oil ash (POA), carbon black (CB) and halloysite nanotubes (HNTs) on the processability, mechanical properties and thermal stability of polypropylene/recycled natural rubber glove (PP/rNRg) composites were studied. The POA based composites showed the lowest processability. The HNTs has a better reinforcement effect compared to POA and CB. HNTs showed a higher tensile strength at 2 phr, whereas POA and CB showed their highest tensile strengths at 4 phr. All fillers reduced the elongation at break but increased the tensile modulus of PP/rNRg composites. The incorporation of POA, CB and HNTs improved the thermal stability of PP/rNRg composites.*

Keywords: Polypropylene, natural rubber, thermoplastic elastomers, palm oil ash, halloysite nanotubes

1. INTRODUCTION

Natural rubber (NR) is an elastomer that has greater flexibility compared to synthetic rubbers. Hence, NR is used to produce various products, including gloves. NR gloves form a barrier with a proven protective capability, which can protect humans from direct contact with blood, body fluids or bacteria. The production of NR gloves has risen to meet the increasing market demand. Consequently, they also pose an environmental problem when they are disposed of. Therefore, this NR glove waste must be managed properly in a manner that does not endanger public health and the environment.[1]

Throughout the recent era, people have also become aware of the importance of recycling polymeric materials. However, the recycling of polymers is not successful because they are difficult to recycle. Some polymers such as thermoset, including NR gloves, are cross-linked. Therefore, it is very important to find an effective method to manage the increasing amount of polymer waste material. On the other hand, the issue of cost is always considered from the economic standpoint when making new materials. The thermoplastic elastomers (TPEs) are a very interesting class of materials that combine the properties of both thermoplastic and elastomers.[2] However, the synthesis of TPEs by using fresh materials has a high cost. Therefore, incorporation of the recycled NR gloves into TPEs is an effective alternative method that can help to solve both cost and environmental issues.

While making TPEs, their properties are very important to ensure they do not easily fail during their service period.[3–5] Thus, fillers are added to enhance the properties of TPEs. In Malaysia, the production and exportation of palm oil has been growing rapidly, subsequently leading to millions of tonnes of oil palm waste annually.[6] 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 palm oil ash (POA). POA is normally dumped into a landfill or a field, causing severe environmental problems.[7] This improper waste management can cause various environmental problems for the country and its people. To solve this problem, palm oil ash should be utilised and turned into a valuable product. More recently, halloysite nanotubes (HNTs) have been revealed to reinforce many polymer matrices.[8] HNTs are unique and versatile nanomaterials that are formed by the surface weathering of aluminosilicate minerals and are composed of aluminium, silicon, hydrogen and oxygen. HNTs are ultra-tiny hollow tubes with diameters typically smaller than 100 nanometres and lengths typically ranging from approximately 500 nanometres to over 1.2 microns.[9]

In this work, POA and HNTs are used as fillers for PP/rNRg composites and are compared with the conventional filler, carbon black (CB). The effects of loading POA, CB and HNTs on the processability, tensile properties and thermal stability of polypropylene/recycled natural rubber glove (PP/rNRg) composites are investigated.

2. EXPERIMENTAL DETAILS

2.1 Materials

The polypropylene (PP) used in this work is PP Grade 6331, which is supplied by Titan Pro Polymers (M) Sdn. Bhd. Johor. The polypropylene has 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, which have a density of 1.015 g/cm^3, are supplied by Juara

One Resources Sdn. Bhd. in Pulau Pinang, Malaysia. The rNRg are first pre-ground by passing them through two roll mills one to two times. The rNRg are then ground by a table type pulverising machine manufactured by Rong Tsong Precision Technology Co., Ltd., Taiwan, until a range of sizes from 117 to 334 μm are obtained. The N330 grade carbon black was supplied by the Cabot Corporation. The particle sizes of the N330 carbon black ranged from 28–36 nm. The POA was collected from United Oil Palm Mill, Pulau Pinang, Malaysia. POA particles were sieved with 75 μm mesh and then dried in a vacuum oven at 80°C for 24 hours to expel moisture. The main elemental composition (wt%) of POA was analysed by an X-ray fluorescence (XRF) spectrometer (model Rigaku RIX3000) and found to be 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). Highly bright and ultrafine grade halloysite nanotubes (HNTs) were supplied by Imerys Tableware Asia Limited, New Zealand, with a brightness of 98.9% as measured by a Minolta CR300 apparatus using a D65 light source. HNTs are ultra-tiny hollow tubes with diameters typically smaller than 100 nanometres and lengths typically ranging from approximately 500 nanometres to over 1.2 microns.[9] Their composition was as follows (wt%): SiO_2 (49.5), Al_2O_3 (35.5), Fe_2O_3 (0.29), and TiO_2 (0.09).[10]

2.2 Processing of the Composites

The formulations of HNT-filled PP/rNRg composites are given in Table 1. All of the materials are melt-mixed with a Haake Rheomix PolyDrive R600/610 Internal Mixer at 180°C with the rotor speed set to 50 rpm. The PP pellets are gradually added into the hopper. The rNRg is added four minutes after the beginning of the process. The weight ratio of PP and rNRg is fixed at 70:30. Next, the fillers are added six minutes after the beginning of the process and then mixing continues for another three minutes. The total mixing time is nine minutes. The composite is later hot pressed for two minutes at 180°C to maintain the dimensional stability of the sample. Then, the composite is cold pressed for three minutes and removed from the mould. Three different types of composites, i.e., PP/rNRg/POA, PP/rNRg/CB and PP/rNRg/HNTs, were prepared.

Table 1: Formulation of filled PP/rNRg composites.

	Materials weight (phr)				
Compounds	PP	rNRg	OPA	CB	HNTs
Control sample	70	30	0	0	–
PP/rNRg/OPA composite	70	30	2	–	–
	70	30	4	–	–
	70	30	6	–	–
	70	30	10	–	–
PP/rNRg/CB composite	70	30	–	2	–
	70	30	–	4	–
	70	30	–	6	–
	70	30	–	10	–
PP/rNRg/HNT composite	70	30	–	–	2
	70	30	–	–	4
	70	30	–	–	6
	70	30	–	–	10

Table 2: The maximum degradation temperature, T_{max}, of filled PP/rNRg composites.

Filler loading (phr)	T_{max} (°C)		
	PP/rNRg/OPA	PP/rNRg/CB	PP/rNRg/HNT
0	465	465	465
2	471	478	469
4	477	479	479
10	478	484	482

2.3 Measurement of the Tensile Properties

The tensile test was carried out by following the ASTM D 638 method with an Instron 3366 testing machine. Dumbell tensile specimens with one mm thicknesses were cut from the moulded sheets with a S6/1/6.A Wallace die cutter. The tensile modulus, tensile strength, and elongation at break were measured at a crosshead speed of 5 mm/min at a temperature of 25 ± 3°C.

2.4 Morphological Study

A Leo Supra-35VP field emission scanning electron microscope (FE-SEM) was used to observe the tensile fractured surfaces of the specimens. First, the fractured surfaces of the specimens were sputter-coated with a thin layer of gold to avoid electrostatic charging and poor resolution. Next, the specimens were mounted onto aluminium stubs for examination.

2.5 Thermogravimetric Analysis

Thermogravimetric analysis (TGA) was performed using a Perkin-Elmer Pyris 6 TGA analyser over a temperature range of 30 to 600°C with a heating rate of 10°C/min under a nitrogen flow of 20 ml/min.

3. RESULTS AND DISCUSSION

3.1 Processability and Torque Development of Filled PP/rNRg Composites

The stabilisation torques of PP/rNRg composites after nine minutes of mixing are shown in Figure 1. Generally, it can be observed that the stabilisation torque value increased with increased filler loading. It is found that the stabilisation torque for the POA-based composite is higher than for the CB- and HNT-based composites, respectively. The POA-based composite shows a lower processability compared to the CB and HNT composites. The major component in POA is silica.[7] Therefore, POA tends to agglomerate due to the silanol groups on its surface. Thus, a higher shear force is needed to break down the POA agglomerates. At similar filler loadings, HNT-based composites have higher stabilisation torque values than CB-based composites. This can be attributed to the particle shape of HNTs. The addition of a high aspect ratio can increase both the viscosity and elasticity of the polymer melt.[11] HNTs have a large aspect ratio, which results in a higher stabilisation torque value of the HNT-based composite compared to the CB-based composite.[8]

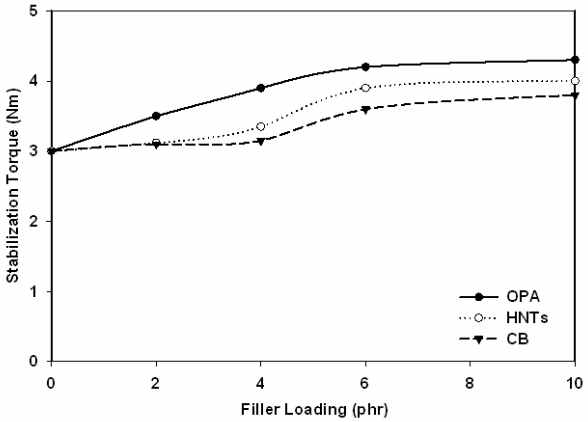

Figure 1: Stabilisation torque of PP/rNRg/OPA, PP/rNRg/CB and PP/rNRg/HNTs composite at ninth minute.

3.2 Tensile Properties of Filled PP/rNRg Composites

The effects of different fillers on the tensile strength of PP/rNRg composites are shown in Figure 2. Generally, the incorporation of a filler can improve the tensile strength of a filled PP/rNRg composite. At 2 phr of filler loading, the HNT-based composite shows the highest tensile strength compared to POA and CB composites. As the filler content increased to 4 phr in the composite, the CB-based composite shows the highest tensile strength followed by the POA-based composite. According to Baccaro et al.[12], the highest tensile strength when a certain amount of carbon black was used might be due to the filler-polymer network. The mechanism of interaction is based on the physical entrapment of the polymeric chains in the carbon black microstructural defects and superficial porosity. All of the composites show a reduction in the tensile strength when the filler loading exceed 4 phr. The HNT-based composite shows the highest tensile strength at 2 phr of filler loading. Du et al.[9] and Liu et al.[13] suggested that the higher tensile strength when adding HNTs can be attributed to the good dispersion of the HNTs in the matrix, the geometrical structure of the HNTs and good filler-matrix interaction. HNTs are a unique and ultra-tiny reinforcing material. With only a small amount of HNTs, a large improvement in the matrix properties can occur leading to lightweight composites.[14]

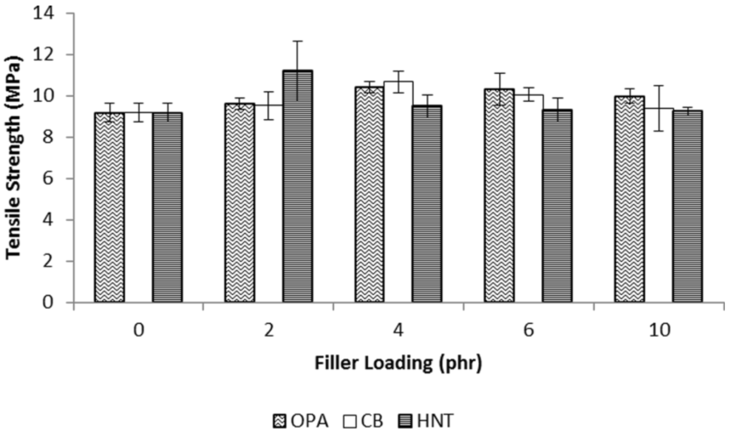

Figure 2: Tensile strength of PP/rNRg composite at different filler loadings.

The results also show that the tensile strength increases as the particle size of the filler decreases. This effect is due to increases in the interfacial area, which can provide more effective interfacial bonds.[15] However, this phenomenon would be accompanied by a tendency for increased agglomeration of the particles. At high filler loadings (6 and 10 phr), all of the composites show a reduction in tensile strength, mainly due to agglomeration. This effect is especially significant for composites filled with smaller filler particles. Therefore, the CB and HNT composites show significant drops in their tensile strengths.

The effects of different fillers on the elongation at break of PP/rNRg composites are presented in Figure 3. Generally, POA, CB and HNT fillers decreased the elongation at break of the composites. The elongation at break of the composites is reduced because the fillers tend to restrict the movement of the polymer chains, which causes the polymer chains to have a low mobility to flow. Hence, the flexibility of the composite is decreased. The addition of fillers such as POA, CB and HNTs increased the tensile modulus of the filled composites (see Figure 4). The tensile modulus of the composite is increased due to the restrictive effect imparted by the filler making it difficult for the polymer chains to flow. Hence, the rigidity of the composite is increased. The opposite result in the tensile modulus of the PP/rNRg/HNTs composite compared to the PP/rNRg/CB and PP/rNRg/POA composites is substantiated by its higher ductility and flexibility, which can be seen from Figure 3. It has been elucidated elsewhere[16–18] that the elongation at break is an inverse function of the tensile modulus; therefore, the characteristics that improve the modulus also act to reduce the elongation at break.

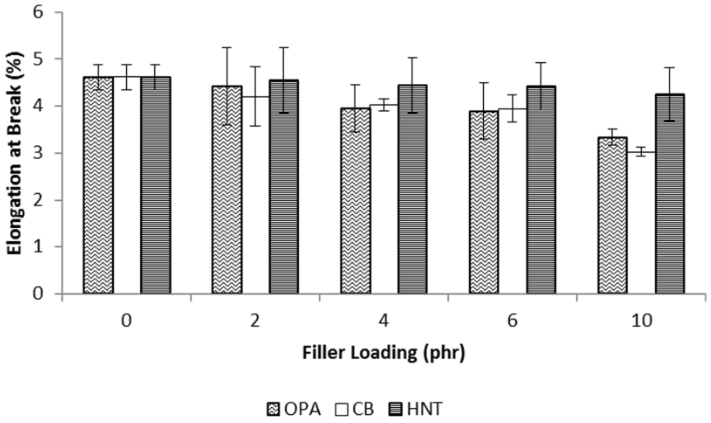

Figure 3: Elongation at break of PP/rNRg composite at different filler loadings.

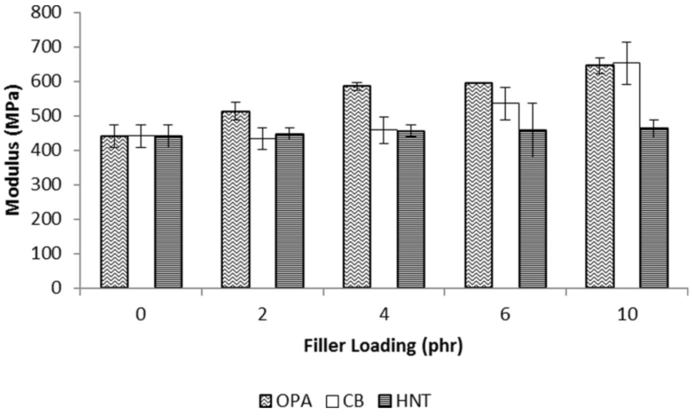

Figure 4: Tensile modulus of PP/rNRg composite at different filler loadings.

It is also observed that the PP/rNRg/HNTs composite showed slightly higher elongation at break than the corresponding PP/rNRg/CB and PP/rNRg/POA composites consecutively. As for the HNT-containing composite, it was elucidated by Yang et al.[19] and Pasbakhsh et al.[8] that the factors influencing the higher elongation at break in HNTs are mainly due to the good dispersion of the HNTs, the intertubular interaction between the HNTs and the polymer matrix, and the homogeneous dispersion of HNTs inside the polymer matrix. These factors are responsible for improving the ductility of the HNT composite compared to the properties of PP/rNRg/CB and PP/rNRg/POA composites, respectively.

Figure 5 shows the morphologies of PP/rNRg composites filled with 4 phr of POA, CB and HNTs, respectively. Comparing Figures 5a, 5b, and 5c reveals how the roughness and the tortuous path of the fracture surface increased when CB was used instead of HNTs or POA. A difference in the matrix tearing lines with a uniform pattern (see Figure 5b) indicated the occurrence of failure in a more difficult manner and resulted in a high tensile strength. The intermediate tensile strength of HNT-filled PP/rNRg composites also corresponds to the SEM observed. Good dispersion of the HNT-filled composite is clearer than in the composite containing POA. The SEM results for the tensile fractured surfaces were in good agreement with the results obtained by Nabil et al.[16], who reported that an increase in energy was responsible for the roughness and the matrix tearing line of the fractured surface.

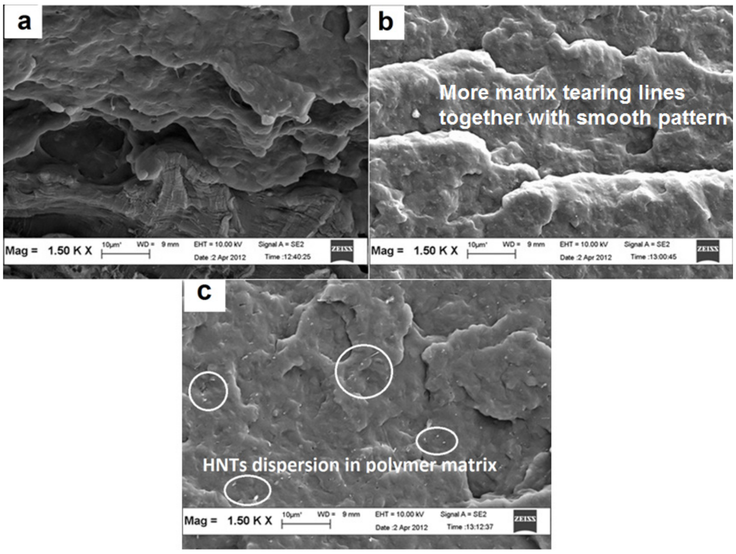

Figure 5: Micrographs of SEM show morphology of PP/rNRg composites filled with 4 phr OPA (a), CB (b) and HNTs (c) respectively (1500× magnifications).

3.3 Thermogravimetric Analysis of Filled PP/rNRg Composites

Table 2 depicts the maximum degradation temperature, T_{max}, of the PP/rNRg composites. It is found that the maximum degradation temperature increased with increasing filler contents. This effect shows that all fillers can function as effective flame-retardant agents. As for POA and HNTs, it can be seen in the materials section that these two fillers are composed of mostly inorganic material. This characteristic can help to improve the thermal stability of the polymer. The improvement of the thermal stability when CB is used is mainly due to the high surface area, structure and surface chemistry. Donnet, Bansal and Wang[20] reported that these three factors are the main reasons leading to the improved thermal stability of the CB-containing composite. All fillers show outstanding properties for improving the thermal stability and flame retardant effects of the composites. The main factor contributing to the improvement of the thermal stability is the barrier effect of the fillers.[6,21–24] The mass transport of degradation product is delayed. Thus, the POA, CB and HNT fillers are expected to be the promising thermal insulation fillers for the composites.

4. CONCLUSIONS

The effects of POA, CB and HNTs on the processability, tensile properties and thermal stability of PP/rNRg composites were comparatively studied. In terms of the processability, the POA-based composites showed the lowest processability. The HNT-based composite has a better reinforcement effect compared to those containing POA and CB. At higher filler loadings (6 phr and 10 phr), the tensile strengths of all of the composites decreased. All fillers reduced the elongation at break but increased the modulus of the PP/rNRg composites. The TGA results showed that POA, CB and HNTs were effective thermal-retardant agents for PP/rNRg composites.

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