Effect of Carbon Black on the Properties of Polypropylene/ Recycled Natural Rubber Glove Blends

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Received: 19 Feb 2015, Accepted: 7 September 2015

SUMMARY

In the present study, recycled natural rubber glove (rNRg) were used in an attempt to create a value-added thermoplastic elastomer material based on polypropylene/recycled natural rubber glove blends. Carbon black (CB) was also incorporated in a way to improve the mechanical properties to the blends. The blends were prepared in an internal mixer where the effects of CB loadings on processability, tensile properties, morphology and thermal stability of the blends were investigated. Results showed that the stabilization torque comparatively increases with the increment of the CB loading. Adding CB also improves the tensile strength and thermal stability to the blends. This is attributed to the better filler-matrix interaction and filler dispersion observed upon the incorporation of CB.

Keywords; Polypropylene; Natural rubber; Thermoplastic elastomers; Carbon black; Blends

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INTRODUCTION

The thermoplastic elastomers (TPEs) industry has increasingly grown and become quite significant in last few decades as the use of TPEs has now reached a high level of commercial importance. TPEs are materials with interesting characteristic because they have the elastic behavior and are re-processable [1-3]. This has brought strong academic interest among the researchers to explore on this line [4]. Low cost and attractive properties such as superior durability, light weight, applicability at elevated temperatures and ability to be tailored for specific engineering applications are some of the prominent properties that may not be available in any other materials [5].

In manufacturing TPEs, natural rubber (NR) is commonly used because it is a durable and highly flexible material [6-8]. NR is successfully used to produce a wide range of industrial applications such as tires, rubber hose, gloves, bridge-bearing and to name a few [6]. Among all these NR products, natural rubber gloves have been one of the fastest growing NR products since its introduction in the past years. The crosslinked natural rubber gloves are thermoset and insoluble, thus it makes the straight reprocessing of natural rubber glove more complicated. This polymeric material cannot return to the ecological environment through biological degradation and is most often discarded after a certain period of time [9].

Recycling of natural rubber gloves is an interesting topic mainly due to the environmental concerns and the continuous market growth of natural rubber glove. As such, scientists are trying to find a satisfactory ways and means to deal with the enormous quantity of such product which is classified as a severe environmental hazard unless they are properly disposed. To solve this issue, considerable attention is based on the effort to create value-added thermoplastic materials based on the recycled natural rubber glove. Therefore, the aim of this study was to use the recycled natural rubber glove as a blending component with polypropylene in making cost-effective TPEs.

Several types of fillers have been used for TPEs, they are incorporated into the compounds for many purposes, e.g., to improve processability, reduce cost, and modify the physical properties of the composites [10-11]. Among commercial fillers, carbon black (CB) is of the most important reinforcing fillers and these are extensively used when high strength is necessary. Thus, attaining the desired properties of PP/rNRg blends can be obtained by incorporating the CB. To the best of our knowledge, no attempt has been made currently on the use of CB in PP/rNRg blends. In the present study, the effects of CB loadings on processability, mechanical properties, thermal stability and morphology of carbon black filled polypropylene/recycled natural rubber glove blends were investigated.

EXPERIMENTAL

Materials

Polypropylene (PP) Grade 6331 with melt flow index of 14 g/10 min at 230°C and density of 0.9 g/cm^3 was supplied by Titan Pro Polymers (M) Sdn. Bhd. Johor, Malaysia. Recycled natural rubber glove (rNRg) with density of 1.015 g/cm^3 was supplied by Juara One Resources Sdn. Bhd., Penang, Malaysia. The rNRg was initially pre-ground by passing through the two-roll mill at room temperature. Next, it was ground into a powder form using a Table Type Pulverizing Machine from Rong Tsong Precision Technology Co. Ltd., Taiwan, to yield a range of particle diameters of approximately 100 to 350 μm. The N330 grade carbon black was supplied by Malayan Carbon (M) Ltd., Malaysia and was used as received.

Preparation of the Blends

The compounding formulation of CB filled PP/rNRg blends are presented in **Table 1**. All the materials were melt-mixed with HAAKE Rheomix PolyDrive R600/610 Internal Mixer at 180°C while the rotor speed was set at 50 rpm. The weight ratio of PP and rNRg was fixed at 70/30 (phr/phr). The PP pellets were added gradually into the hopper and the rNRg was added after 4 min of mixing. Subsequently, the mixing was continued for another 2 min, the CB was then added and left to melt for 3 min. The total mixing time was 9 min. The blend was later hot-pressed for 2 min at 180°C in order to maintain the dimension stability of the sample. Finally, the blend was cold-pressed for 3 min prior to remove it out of the mould.

Table 1. Formulation of CB filled PP/rNRg blends

Materials	Composition (phr)
Polypropylene (PP)	70
Recycled Natural Rubber Gloves (rNRg)	30
Carbon Black, N330 (CB)	0, 2, 4, 6, 10

Measurement of Tensile Properties

Dumbbell-shaped samples were cut from the molded sheets with a Wallace die cutter, S6/1/6.A according to ASTM D 638. Tensile tests were performed at a cross-head speed of 5 mm/min with a universal tensile machine (Instron 3366) to determine the tensile properties in terms of tensile modulus, tensile strength, and elongation at break.

Scanning Electron Microscopy (SEM)

The examination of tensile fractured surfaces was carried out by using scanning electron microscope (Leo Supra-35VP FE-SEM), to obtain information on the possible presence of microdefects. The fractured pieces were coated with a layer of gold palladium to eliminate electrostatic charge build up during examination.

Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) was carried out with a PerkinElmer Pyris 6 TGA analyzer. The sample was scanned from 30° to 600°C under the nitrogen flow of 20 ml/min with a heating rate of 10°C/min.

RESULTS AND DISCUSSION

Processability and Torque Development of CB Filled PP/rNRg Blends

Figure 1 shows the torque values development for PP/rNRg blends having different CB loadings. Generally, PP is firstly added into the mixing chamber and rotors are started. The torque initially rises sharply due to the resistance exerted on the rotors by the unmelted PP. As PP melts and subjects to mechanical shearing the torque drops and become stable. The torque increases sharply again when rNRg is charged into the mixing chamber after 4 min of mixing.

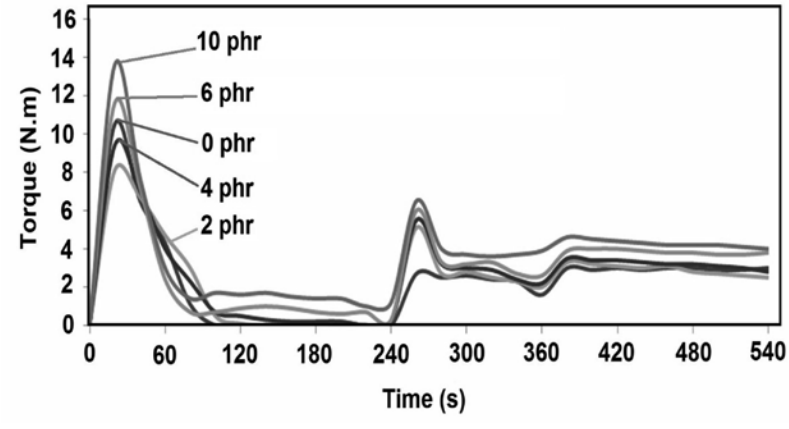

Figure 1. *Torque development for CB filled PP/rNRg blends*

Subsequently, similar observation was recorded as rNRg dispersed in the PP matrix. Finally, the torque slightly increases again due to the addition of CB after 6 min of mixing and equilibrium torque was achieved when the blends become homogenized.

The stabilization torque at 9th min of mixing is shown in **Figure 2**. The stabilization torque indicates the attainment of a stable structure after achieving a good level of mixing. It was observed that the stabilization torque decreases at the lower amount of CB loadings e.g., 2 and 4 phr when compared to the unfilled blend but it increases upon the addition of CB. Lower stabilization torque found at 2 and 4 phr of CB may be due to the well dispersion of CB at low loadings which causes the reduction in viscosity when mixing with high viscosity PP. In contrast, the higher stabilization torque observed for 6 and 10 phr of CB loadings, is simply attributed to the agglomeration of CB which increases the shearing force to produce the composites. This observation is in agreement with the previous report on the blends based on PP/rNRg in the presence of oil palm ash [12].

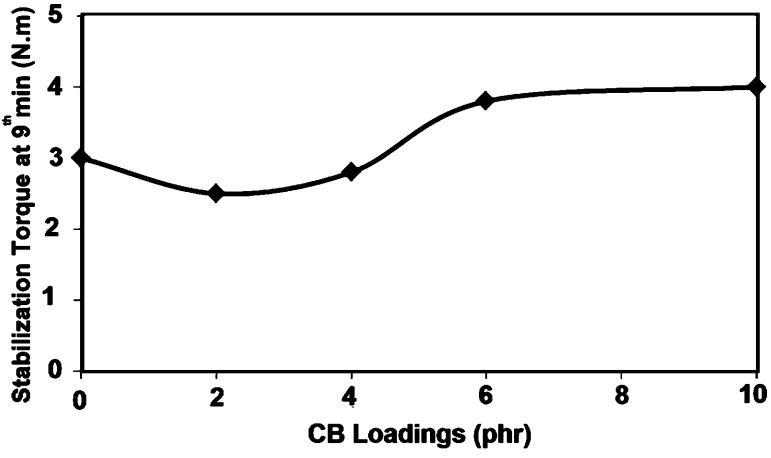

Figure 2. *Stabilization torque at 9th minute of CB filled PP/rNRg blends*

Tensile Properties of CB Filled PP/rNRg Blends

The tensile strength of PP/rNRg blends as a function of CB loadings is shown in **Figure 3**. The improvement of tensile strength is more evident as CB content increases up to 4 phr, then decreases. The percentage increments of tensile strength at 4 phr of CB content over the unfilled blend is 16.4% (9.17 – 10.67 MPa) while the percentage increment of tensile strength at 10 phr of CB content over the unfilled blend is 2.3% (9.17 – 9.38 MPa).

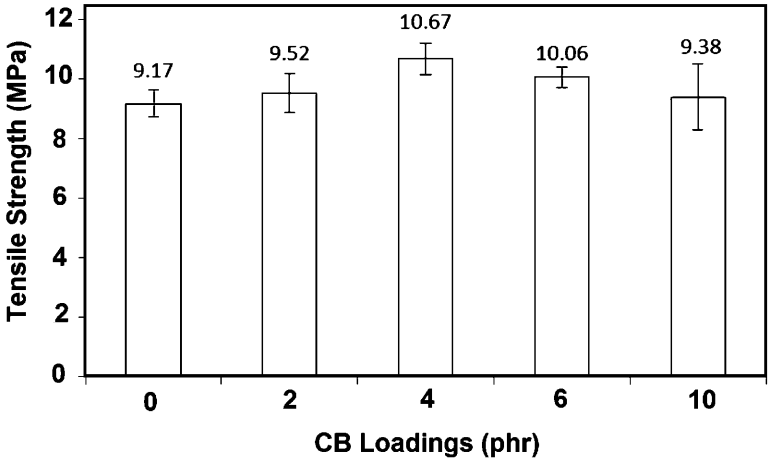

Figure 3. *Tensile strength of CB filled PP/rNRg blends*

The increment of tensile strength in CB filled PP/rNRg blends can be explained by two factors. Firstly, it is due to the reinforcing nature of filler itself [13]. The reinforcing ability of filler is measured by its carbon content [14]. According to Baccaro et al. [15], higher reinforcement in the case of carbon black content might be due to the physical entanglement. The filler-polymer interaction mechanism is based on the physical entrapment of the polymeric chains in the carbon black microstructure defects and superficial porosity. Thus, the CB has great reinforcing ability. Secondly, it is supposed to be due to the CB is well-dispersed in the matrix which is shown in SEM results in the latter section. The CB aggregates that composed of tightly packed primary particles displayed higher level of polydispersity compared to primary particles [16]. Besides, the better CB aggregates-matrix interaction is also observed. The PP chains entangle into aggregates through the voids between the primary CB particles. The filler-matrix interfacial area is enhanced, thus leading to improve the tensile properties of CB filled PP/rNRg blends.

The decline in tensile strength with further increase of CB concentration is due to the agglomeration of CB. Previous researchers emphasized that mechanical properties of composite are easily influenced by the filler particles agglomeration [17]. The agglomeration of CB is attributed to the ineffective dispersion of CB which causes the formation of stress concentration spots, voids or cracks in the blends and resulting to lower the tensile strength eventually [11].

Figure 4 presents the elongation at break of PP/rNRg blends with different CB loading. It was found that the elongation at break of CB filled PP/rNRg blends decrease with increasing CB loadings. When the PP chains are entangled

and trapped in the voids of CB aggregates, the PP chains become highly immobilized [15]. Thus the elongation at break of blends decreases. Another relevant reason can be explained by the agglomeration of CB which formed irregularity of chain rearrangement that producing difficulty in recrystallization during deformation, leading to lower the elongation at break upon the addition of CB. As for the tensile modulus, it can be seen in **Figure 5** that tensile modulus increases with increasing of CB loadings. The CB particles embedded in the PP matrix act as hindrance which reduces the mobility of PP chains. The chains become stiff, resulting to increase the tensile modulus of PP/rNRg blends.

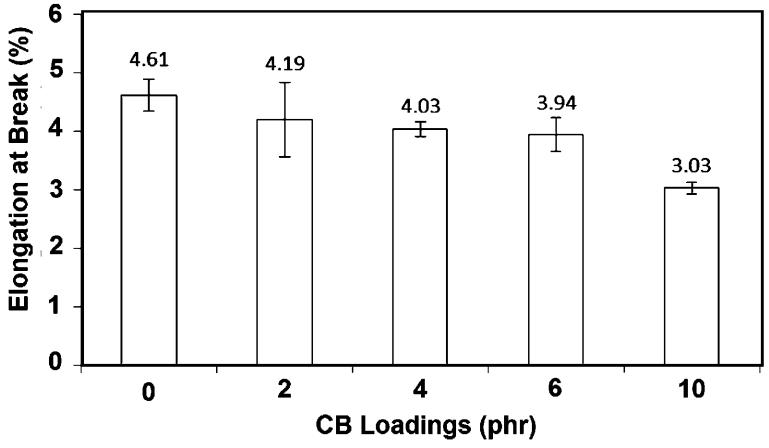

Figure 4. *Elongation at break of CB filled PP/rNRg blends*

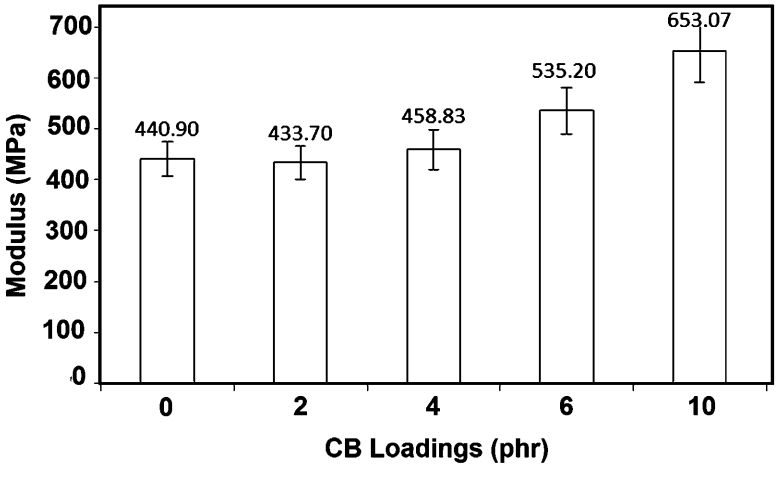

Figure 5. *Tensile modulus of CB filled PP/rNRg blends*

Micro-fractured Surfaces of CB Filled PP/rNRg/CB Blends

Figures 6A-D and **7A-B** show the SEM micrographs of tensile fractured surfaces of PP/rNRg blends. The morphology of an unfilled PP/rNRg blend is shown in **Figure 6A**. It is clear that the rNRg was well-embedded in the PP matrix due to good interaction between the rNRg and PP. **Figure 6B-D** shows the tensile fractured surface of PP/rNRg blend filled with 4 phr of CB. It can be seen that the CB is embedded strongly in the matrix, exhibited by the fact that there is no gap around the CB. Furthermore, well-dispersed and uniformly distributed CB in the blend is more evident at the higher magnifications as shown in **Figure 6C-D**, the fractured surface shows no sign of filler agglomeration or filler pull-out of the matrix. Good adhesion between CB and polymer matrix leads to better stress transfer across the interface. The CB can support the stress transferred from the matrix As a result, better tensile strength of PP/rNRg blend is observed.

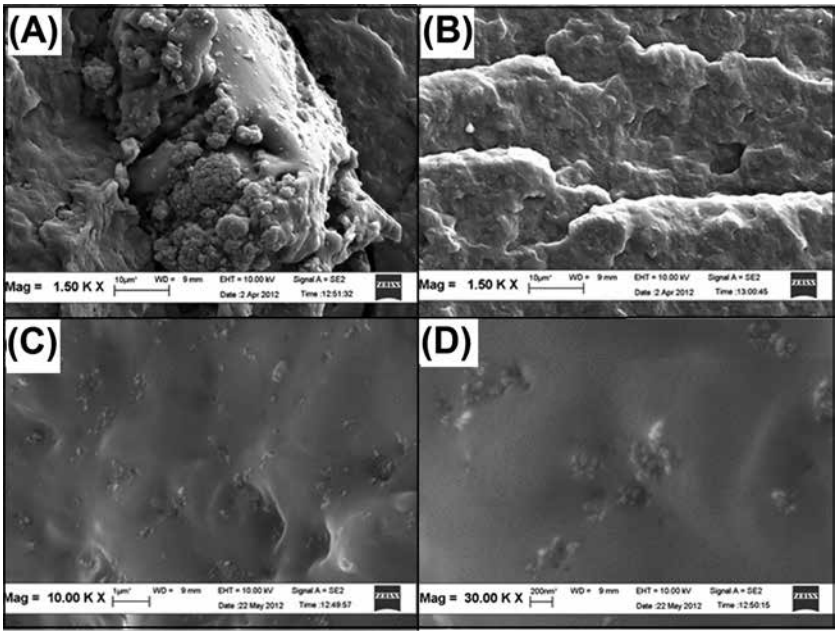

Figure 6. *SEM micrographs of unfilled PP/rNRg blend (A) and PP/rNRg blend at the loading of 4 phr of CB under 1500× magnifications (B), 10000× magnifications (C) and 30000× magnifications (D)*

As mentioned in the preceding section that the decline in the tensile strength of the blend (e.g., 10 phr of CB loading) is due to the agglomeration of CB. This can be spotted by its respective tensile fractured surface. As shown in

Figure 7A, agglomeration is formed by aggregates which are held together by van der Waals forces. The presence of CB agglomerations lead to the high stress concentration formed around the particles themselves making the matrix easy to fail [17]. This can be clearly seen at the higher magnification (**Figure 7B**), showing that clear indication of filler agglomeration is observed at higher loading of CB.

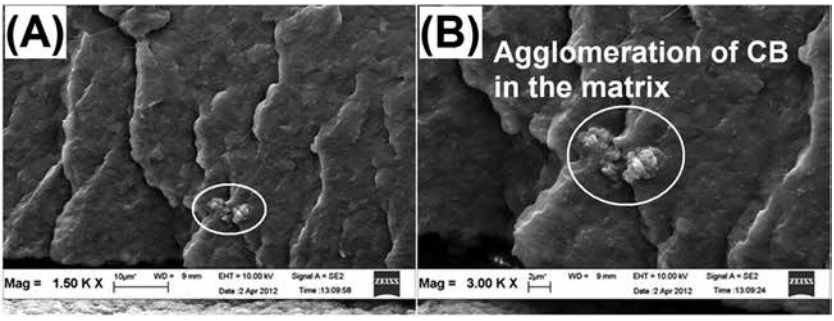

Figure 7. *SEM micrographs of CB filled PP/rNRg blends at the loading of 10 phr of CB; 1500× magnifications (A) and 3000× magnifications (B)*

Thermogravimetric Analysis of CB Filled PP/rNRg Blends

Thermogravimetric analysis is one of the commonly used techniques for rapid evaluation of thermal stability, and also indicates the decomposition of polymers at various temperatures. **Figure 8** shows the TGA curves of CB filled PP/rNRg blends. The decomposition temperatures at 5%, 50% (T_5 and T_{50}) and maximum weight loss (T_{max}) and the amount of char residue are tabulated in **Table 2**. The decomposition temperature at 5% and 50% weight loss of the blends was influenced by the CB loadings. During the thermal degradation, the TGA curves are shifted to the higher temperature in decomposition region which indicate the increasing of thermal stability of blends. The unfilled blend started to show thermal degradation (5% weight loss) at 332.83°C, then 50% weight loss at 444.60°C and fully decomposed without any residue left at 583°C. As for 2 phr of CB loading, it began to degrade (5% weight loss) at 381.01°C and later 50% weight loss at 468.77°C. The blend shows 14.5% and 5.4% thermal stability improvement when compared to unfilled blend. The increment of the decomposition temperature is more prominent when the PP/rNRg blend is filled with 10 phr of CB, the T_5 and T_{50} were 416.29°C and 479.10°C respectively which is approximately 9.2% and 2.2% higher than that of unfilled blend. This implies that CB has great influence on the thermal stability of the blends.

Table 2. The decomposition temperatures at 5%, 50% and maximum weight loss and the char residue for PP/rNRg blends at various CB loadings

Samples	T_5 (°C)	T_{50} (°C)	T_{max} (°C)	Char residue (%)
CB 0 phr	332.83	444.60	465.06	0
CB 2 phr	381.01	468.77	478.65	2.33
CB 4 phr	408.32	473.36	479.10	6.30
CB 10 phr	416.29	479.10	483.71	11.30

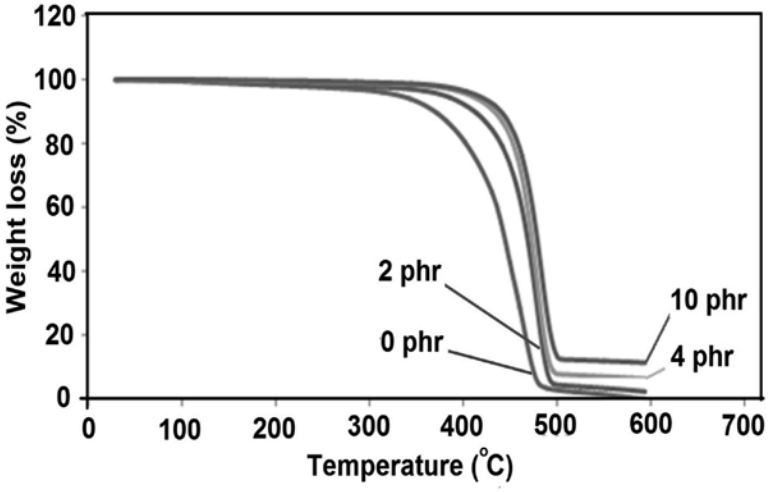

Figure 8. *The TG curve of CB filled PP/rNRg blends*

This may be associated to the nature of CB itself; Roy et al. [18], has proposed that the higher surface area of filler itself is prominently responsible for the reduction of thermal motion of polymer chains within the network structure, resulting in improving the thermal stability of the blends.

Table 2 also illustrates the decomposition temperature at maximum weight loss and char residues of the blends derived from TG profiles. Significantly, incorporating CB enhances thermal stability by shifting the decomposition temperature upwards. This is simply due to CB having higher surface area, which provided higher contact to the matrix and restricted molecular motion; therefore, a higher temperature is required to cleave the linkages [17, 19]. Furthermore, the char residue of all blends was influenced by the presence of CB. In this experiment, the analysis was conducted under nitrogen atmosphere, this causes the CB remained unchanged because of its inertness under nitrogen atmosphere, thus keeping the char residue mostly different. It was also found that the char residue increases with increasing the CB. According

to Chakraborty et al. [20], the amount of char residue is very much dependent on the types and amount of filler or inorganic additives. The difference in CB content mainly affects the amount of char formation.

CONCLUSIONS

It was clearly shown that the recycled natural rubber gloves were used in an attempt to create a value-added thermoplastic elastomer material based on polypropylene/recycled natural rubber glove blends in the presence of carbon black (CB). From the above mentioned results, it was found that the stabilization torque and tensile modulus of the blends increase with increasing CB loading whereas elongation at break shows an opposite trend. Besides, the blends show that the tensile strength increases up to 4 phr of CB, beyond that, it decreases upon the addition of CB. The optimum tensile strength observed could be due to the well-dispersed CB in the matrix where it is further verified by SEM micrographs, showing more surface roughness observed at this loading. Adding CB also shows that decomposition temperature at different stages of weight loss and char residues have shifted to higher temperature, indicating more thermal stability of blends are found upon CB loadings. In summary, it can be concluded that the addition of CB at 4 phr to the PP/rNRg blend is highly recommended when high strength is essential.

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