Effect of Copper Grafted Graphite Loading on Cure Characteristics of Natural Rubber Composites

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Abstract

Metal-coated graphite-based materials are important to effectively transmit and control heat for different electrical and electronic applications. In this study, copper grafted graphite (Cu-g-graphite) was synthesized according to a chemical process and, six natural rubber (NR) composites were prepared by varying the Cu-g-graphite loading from 2 parts per hundred parts of rubber (phr) to 10 phr at 2 phr intervals. Maximum torque and delta cure results indicated high cross-link density for the composites prepared with Cu-g-graphite. In contrast, the stock viscosity of the composites decreased with the increase of the Cu-g-graphite loading. Further, the composite prepared with 10 phr loading of Cu-g-graphite showed the highest scorch time indicating the highest processing safety. However, cure time slightly increased with the increase of Cu-g-graphite loading and, slower cure rate was indicated at higher Cu–g-graphite loading. Overall, the composite prepared with 10 phr loading of Cu-g-graphite which exhibited higher scorch safety and crosslink density compared to the others would be suitable for particular dry rubber-based applications.

Keywords: Cu-g-graphite, natural rubber, minimum torque, cure time, cure rate index

I. INTRODUCTION

Modified graphite incorporated polymer-based materials are a major topic today due to their excellent chemical, physical, rheological and mechanical properties. Generally, rubber-based polymeric materials are limited to many applications in many industries due to their inherent properties. However, rubber-based materials are shown in good demand for mechanical applications due to their high visco-elastic properties, as well as their durability and ease of processing (Nasir et al., 2015). In contrast, the thermal conductivity of rubber is poor and, hence it has poor heat diffusion through rubber matrix. Therefore, most of the research is focused on developing rubber-based materials with high thermal stability and high mechanical properties as a solution to the problems stated earlier (Allaoui et al., 2002; Zou et al., 2009). Literature suggests that, the thermal conductivity of rubber-based materials could be increased by adding certain additives. There are different types of fillers that have been used for such composite processing. Some of them are carbon black (CB), graphite, carbon fiber, carbon nanotube (CNT), pure metal, metal-coated inorganic particles, metal powders, etc. (Das et al., 2000, 2002; Zou et al., 2009). However, the most commonly used material for rubber is CB as it provides better chemical, physical, rheological and mechanical properties as well as good reinforcement to the rubber matrix (Roland, 2016). In this study, copper grafted graphite was used as a filler material since natural graphite poorly disperses in the rubber matrix and, raw graphite particles are chemically inert with the polymer matrix (Ulfah et al., 2015). Further, air voids will be formed around the graphite particles. Additionally, to achieve higher thermal conductivity at lower loading, metal-coated graphite-based materials such as copper-coated, silver-coated and nickel-coated graphite-based filler may be a better choice than raw graphite. Further, metal grafted graphene was used to improve electron field emission and increase the density of the end composite (Kaushik et al., 2013). Metal-coated graphite-based materials are very important to effectively transmit and control heat for application performances (Jang et al., 2017). In this study, Cu-coated graphite powder was fabricated according to a chemical-reaction process (Jang et al., 2017) and, the study concentrates on the cure characteristics of Cu-g-graphite powder-filled NR composites.

II. METHODOLOGY

A. *Preparation of Cu-g-graphite/ NR composites*

A series of NR composites was formulated by varying the Cu-g-graphite loading from 2 phr to 10 phr at 2 phr intervals. The NR composite prepared without Cu-g-graphite was considered as the control. The formulation of the composites is given in Table 1. The composites were prepared by melt mixing using a Brabender Plasticorder operated at room temperature, at a rotor speed of 60 rpm. Total mixing time was kept constant at 10 min.

Table 1: Formulation of the Cu-g-graphite/ NR composites

Ingredient	Function	Phr
Natural rubber	Rubber	100
ZnO	Inorganic activator	5.0
Stearic acid	Organic co-activator	2.0
TMQ	Antioxidant	1.0
Cu-g-graphite	Filler	0,2,4,6,8,10
ZDC	Accelerator	1.5
Sulphur	Vulcanizing agent	2.0

B. *Cure characteristics*

Cure characteristics of Cu-g-Graphite/NR composites, such as minimum torque, maximum torque, scorch time, optimum cure time (T_{90}), cure rate index (CRI), and extent of cure or delta cure (M_H - M_L), were obtained by a Dynamic Rubber Process Analyzer (D-RPA 3000- MonTech, Germany) at 150 ºC.

III. RESULTS AND DISCUSSION

A. *Cure characteristics of Cu-g-graphite/ NR composites*

Rheographs provide important characteristics namely, scorch time, cure time, minimum torque, maximum torque, delta cure and cure rate of a rubber composite. The scorch time (t_{s2}) is usually defined as the onset of vulcanization of a composite at a specific temperature, which represents the time limit available for processing. Cure time (t_{90}) is the time required for 90% vulcanization of the composite to achieve the required degree of cross-linking to yield the desired properties. The minimum torque (M_L) is mainly related to the processability and viscosity of the unvulcanized stock. The rheographs of Cu-g-graphite/ NR composites are shown in Figure 1. According to these curves, the composites prepared with 6 phr, 8 phr and 10 phr Cu-g-graphite show similar patterns, but they differ from the curves of the other three composites.

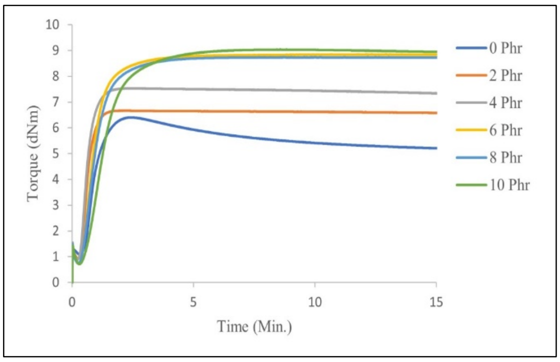

Figure 1. Rheographs of Cu-g-graphite/NR composites

B. *Minimum Torque (M_L)*

Minimum torque is an indication of stock viscosity and processability of rubber composites (Ismail et al., 2002). As shown in Figure 2, the minimum torque values of the composites decrease with the increase of the Cu-g-graphite loading. The results obtained show the highest value for the control (without Cu-g-graphite) composite and the other composites show significant similarities from 2 phr to 10 phr. The main reasons for this may be wettability and the low density of graphite-based material (Ismail et al., 2011). Further, lower minimum torque indicates a lower viscosity and it may be due to better dispersibility of filler and low force requirement for the torque generated initially (Ismail et al., 2011). Hence, the composite prepared with 10 phr loading of Cu-g-graphite shows the lowest minimum torque and indicates the lowest viscosity in comparison to the other composites.

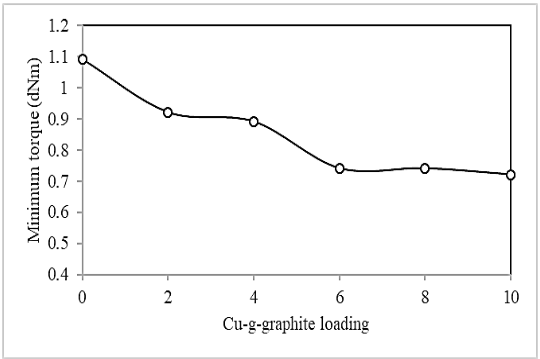

Figure 2. Variation of minimum torque of Cu-g-graphite/NR composites

C. *Maximum Torque (MH)*

Maximum torque is an indication of the state of cure (Surya et al., 2018). Further, maximum torque may give an idea of the maximum extent of curing such as crosslink density and the static/ shear modulus or the hardness of the fully vulcanized compound (Charoeythornkhajhornchai et al., 2017). As shown in Figure 3, the maximum torque values of the composites increase with the increase of the Cu-g-graphite loading and the highest M_H value is exhibited by the composite prepared with 10 phr Cu-g-graphite. It can be due to the improved reinforcing efficiency, better dispersion and distribution of filler in the NR composites and greater cross-link density (Teh et al., 2004). Furthermore, the gradual addition of Cu-g-graphite loading facilitates the generation of cross-linkers, which in turn increases the rigidity or toughness of the composite.

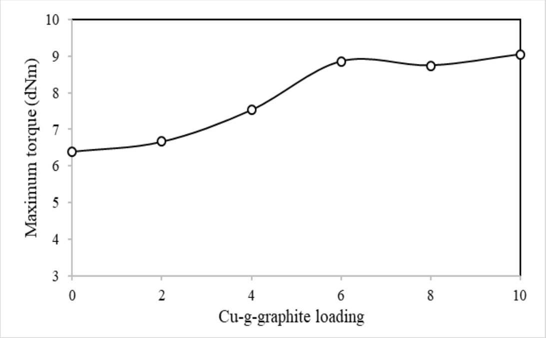

Figure 3. Variation of maximum torque of Cu-g-graphite/NR composites

D. *Delta Cure (MH- ML)*

M_H- M_L torque is an indication of the cross-link density of rubber compounds (Surya et al., 2018). As shown in Figure 4, when the loaded amount of Cu-g-graphite powder increases, the delta cure value increase compared to the control composite and the highest torque value is shown by the composite prepared with 10 phr loading of Cu-g-graphite. This indicates that the incorporation of filler into the rubber matrix leads to higher viscosity and modulus of rubber composites (Ngamsurat et al., 2011). The increase of this torque value is consistent with the known behavior of increasing viscosity with the addition of carbon. Delta cure is generally related to the cross-link density of NR composites. An increase in the value of delta cure indicates an increase in cross-link density (Surya et al., 2013). Hence, an increase in cross-link density with the increase of Cu-g-graphite loading may have caused the delta cure values of the composites to increase as shown in Figure 4.

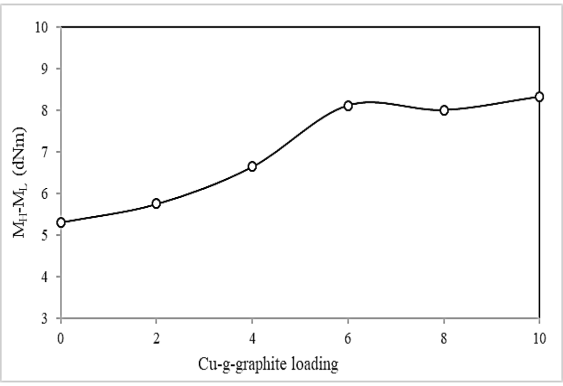

Figure 4. Variation of M_H- M_L of Cu-g-graphite/NR composites

E. *Scorch Time (ts2)*

The variation of scorch time of the composites with Cu-g-graphite loading is shown in Figure 5. These values give information about the premature cure for processing safety. According to Figure 5, the addition of Cu-g-graphite from 2 phr to 10 phr shows an increasing trend in the scorch time. This improvement may result as a consequence of the change in filler parameters such as higher surface area, surface reactivity, particle size, and moisture content (Ismail et al., 2011). When compared with the control composite, only the composite prepared with 10 phr loading of Cu-g-graphite shows a higher scorch time. In general, scorch time decreases due to the restriction of mobility and deformability of the matrix with the introduction of mechanical restraints (Pornprasit et al., 2016). Therefore, the lower values obtained for the composites prepared with 2 phr to 8 phr Cu-g-graphite could be attributed to the above reasons.

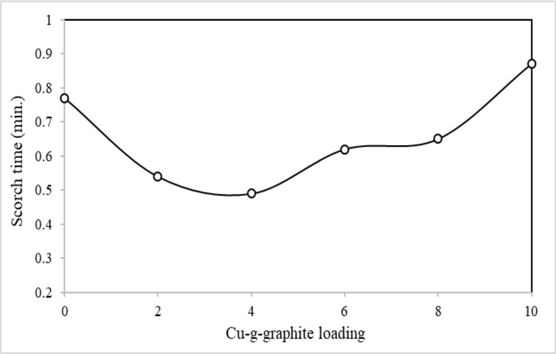

Figure 5. Variation of scorch time of Cu-g-graphite/NR Composites

F. *Cure Time (t90)*

The cure time (t_{90}) is the required time during the step of vulcanization for need the required amount of cross-linking to occur, yielding the desired properties. Figure 6 shows the 90% curing time of Cu-g-graphite/ NR composites. According to Figure 6, by adding Cu-g-graphite from 2 phr to 10 phr, the cure time is increasing gradually. Most of the time, this improvement is a consequence of filler parameters such as higher surface area, surface reactivity, particle size, and moisture content (Ismail et al., 2011). However, according to Figure 6, when adding Cu-g-graphite powder at 2 phr and 4 phr, shows a lower curing time compared to the control composite. These results could be caused due to the increasement in viscosity of former composites (Pornprasit et al., 2016).

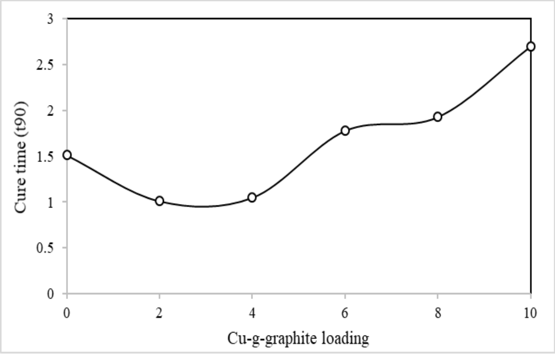

Figure 6. Variation of cure time of Cu-g-graphite/NR composites

G. *Cure rate index (CRI)*

The Cure Rate Index (CRI) is a measurement of the cure rate of composite based on the difference between the optimal cure time (t_{90}) and the initial scorch time (t_{S2}). According to Figure 7, The CRI values of the Cu-g-graphite filled NR composites are lower than that of the control composite. However, there is no significant variation between the cure rate of composites prepared from 6 phr to 10 phr loading of Cu-g-graphite as the variation is between 12.01 min^{-1} and 12.32 min^{-1}. A faster cure rate index has been reported for fillers having lower surface area (Nair et al., 2012). A Moderate increment of the cure time with the loading of graphite indicates a slight increase in production time. In addition, the slight delay in vulcanization at higher filler loadings is a known effect in rubber vulcanization (Shanmugharaj et al., 2019).

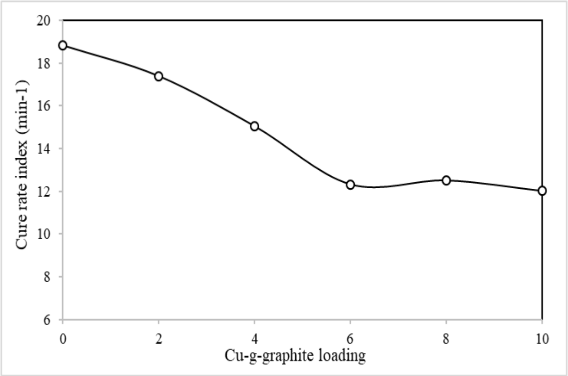

Figure 7. Variation of cure rate index of Cu-g-graphite/NR composites

IV. CONCLUSIONS

The composite prepared with 10 phr loading of Cu-g-graphite shows better cure characteristics in terms of maximum torque, delta torque, scorch time, etc. The finding of this study is Cu-g-graphite powder could have a retarding effect on the accelerator, which in turn can slow down the sulphur vulcanization process leading to an increase in cure time. Further, the composites prepared with Cu-g-graphite indicate low energy combustion due to the low cure time exhibited. Hence, results suggest that the reduction of cure time of Cu-g-graphite incorporated NR composites would be an advantage for high-energy combustion rubber-based processes such as in the case production of solid tires.

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