Influence of Magnesium Carbonate Loading on the Compound Properties of Polychloroprene, Natural Rubber, and Their Blends

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ABSTRACT: The effect of magnesium carbonate ($MgCO_3$) loading on the compound properties of polychloroprene (CR), natural rubber (NR), and their blends was investigated. The studied properties included Mooney viscosity, cure characteristics, and degree of filler–filler interaction. In addition to $MgCO_3$ loading, the effect of the blend ratio on such properties was simultaneously determined. The results reveal that, regardless of the rubber type and blend ratio, increasing $MgCO_3$ loading resulted in not only an increase in the compound viscosity, but also in the enhancements of the cure rate and state of cure. However, the effect of $MgCO_3$ loading on the overcured behavior was strongly dependent on the rubber type and blend ratio. For CR, the presence of $MgCO_3$ accelerated postcuring, whereas the opposite results were found for NR, in which the reversion rate was promoted. For CR/NR blends, a plateau behavior was obtained at a 50/50 blend ratio, where the degrees of postcuring and reversion were counterbalanced. The results also reveal that when $MgCO_3$ was loaded at low concentrations ($\leq$20 phr), the degree of filler–filler interaction was very low and had no significant effect on the compound properties. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 2763–2769, 2008

Key words: blends; curing of polymers; fillers; rubber

INTRODUCTION

Magnesium carbonate ($MgCO_3$) is classified as a semi-reinforcing filler mainly used for cost reduction in light-colored products in which a high strength is not essential. It is used in natural rubber (NR) for a number of reasons, including the improvement of processability and the attainment of particular specifications, such as density, color, and even price. It has also been reported that $MgCO_3$ could improve the incorporation and dispersion of silica in NR during mixing; that is, the dosage of silane coupling agent necessary to achieve the required properties could be reduced in the presence of $MgCO_3$.[1] Apart from being a good absorber for many chemicals, such as petroleum oil, $MgCO_3$ is also added to some polymers, such as polychloroprene (CR) and chlorosulfonated polyethylene (CSM), for smoke-suppression purposes during combustion.[2–5] Moreover, $MgCO_3$ can also act as an acid acceptor, and is more active than magnesium oxide (MgO), for reducing the amount of hydrogen fluoride released from fluoroelastomers.[6] However, it was reported that, unlike MgO, $MgCO_3$ cannot function as a stabilizer or acid acceptor in CR.[7,8]

Recently, many researchers have focused their work on the properties of NR/CR blends;[9–11] however, very little attention has been given to the properties of CR/NR blends filled with $MgCO_3$. As a result, the objective of this research was to investigate the influence of $MgCO_3$ loading on some properties, such as the compound viscosity, cure characteristics, and degree of filler–filler interaction, of CR, NR and their blends.

EXPERIMENTAL

Materials

The details of the compounding ingredients and rubber formulation used in this study are given in Table I.

Preparation and testing of the rubber compounds

CR and NR were initially blended in a laboratory-size internal mixer (Brabender plasticorder, Duisburg, Germany) equipped with cam rotors. The

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TABLE I
Compounding Ingredients and Rubber Formulations Used in This Study

Material	Grade/supplier	Loading (phr)
CR	Neoprene W/Dupont Dow Elastomers PTE, Ltd. (Wilmington, DE)	Variable[a]
NR	STR 5L/Union Rubber Products Co., Ltd. (Bangkok, Thailand)	Variable[a]
MgCO$_3$	Commercial/Konoshima Chemical Co., Ltd. (Osaka, Japan)	Variable[b]
ZnO	Commercial/Chemmin Co., Ltd. (Bangkok, Thailand)	3
Stearic acid	Commercial/Chemmin Co., Ltd. (Thailand)	2
Sulfur	Commercial/Chemmin Co., Ltd. (Thailand)	2
Ethylene thiourea	ETU 22S/Kawakushi Chemical Industry Co., Ltd. (Saitama, Japan)	0.3
N-tert-Butyl-2-benzothiazole sulfenamide	Santocure TBBS/Reliance Technochem (Flexys) Co., Ltd. (Bangkok, Thailand)	1

[a] The blend ratio of CR to NR was varied: 100/0, 75/25, 50/50, 25/75, and 0/100.
[b] The MgCO$_3$ loading was varied: 0, 5, 10, 15, and 20 phr.

mixing conditions were set as follows: fill factor = 0.7, initial chamber temperature = 60°C, and rotor speed = 40 rpm. After 1 min, all chemicals [i.e., zinc oxide (ZnO), stearic acid, N-tert-butyl-2-benzothiazole sulfenamide, ethylene thiourea (ETU), sulfur, and MgCO$_3$] were added to the mixer and were mixed further for 5 min. Finally, the rubber compounds were dumped, sheeted on a two-roll mill and kept at room temperature for 24 h before testing. After mixing, the measurement of the Mooney viscosity of the rubber compounds was carried out with a Mooney viscometer (TechPro viscTECH+, Cuyahoga Falls, OH) according to the method described in ISO R289. The cure characteristics were determined at a test temperature of 155°C with a moving die rheometer (TechPro MD+) according to the method described in ISO 6502. The vulcanization rate was determined from the slope of the cure curve during the curing period. Both marching and reversion rates were also determined from the slope of the cure curve during the overcured period. A rubber process analyzer (RPA2000, Alpha Technologies, Akron, OH) was used to investigate the extent of filler–filler interaction. The test was carried out at a temperature and frequency of 100°C and 1.7 Hz, respectively. The elastic modulus (G′) of the rubber compounds was measured at various strains ranging from 0.98 to 200.04%. The difference in G′ (ΔG′) at low and high strains, widely known as the Payne effect, was used to indirectly represent the degree of filler–filler interaction.[12–14]

To compare the degree of filler–filler interaction between MgCO$_3$ and silica (SiO$_2$), we carried out an additional experiment by replacing MgCO$_3$ with SiO$_2$ (Hisil 255s, Tokuyama Siam Silica, Co., Ltd., Rayong, Thailand). After compound preparation, ΔG′ of the SiO$_2$-filled compounds was determined and then compared with that of the MgCO$_3$-filled compounds.

RESULTS AND DISCUSSION

Figure 1 shows the effect of the MgCO$_3$ loading on Mooney viscosity of CR, NR, and their blends. Obvi-

ously, for all of the compounds, the Mooney viscosity increased continuously with increasing MgCO$_3$ loading. This was easily understandable because MgCO$_3$ is a nondeformable solid, and thus, increasing the MgCO$_3$ loading gave rise to the reduction of the deformable rubber portion in the compound; this is widely known as the dilution effect. The addition of MgCO$_3$, therefore, restricted the flow of rubber compound and resulted in an increase in viscosity. It was observed that, at a given loading, NR possessed a higher viscosity than CR, probably because of its higher molecular weight. Surprisingly, we found that the viscosity of the CR/NR blend did not follow the mixture's rule; that is, its viscosity was lower than that of the individual blend partner. Such negative deviation is attributed to high incompatibility of the blend partners. Because of the dilution effect, the viscosity of the CR/NR blend tended to increase with increasing NR content.

The cure curves of CR, NR, and their blends are given in Figure 2. Regardless of the MgCO$_3$ loading, marching behavior (i.e., an unlimited rise of torque with time after complete cure) was observed for neat CR and the 75/25 CR/NR blend. Contrary results
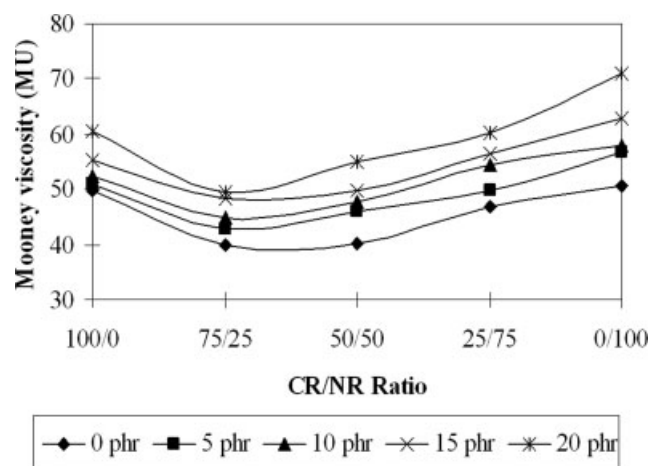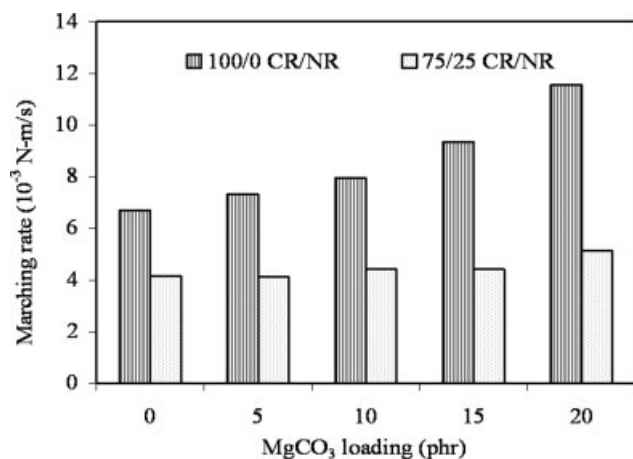

Figure 1 Effect of the MgCO$_3$ loading on the Mooney viscosity of CR, NR, and their blends.
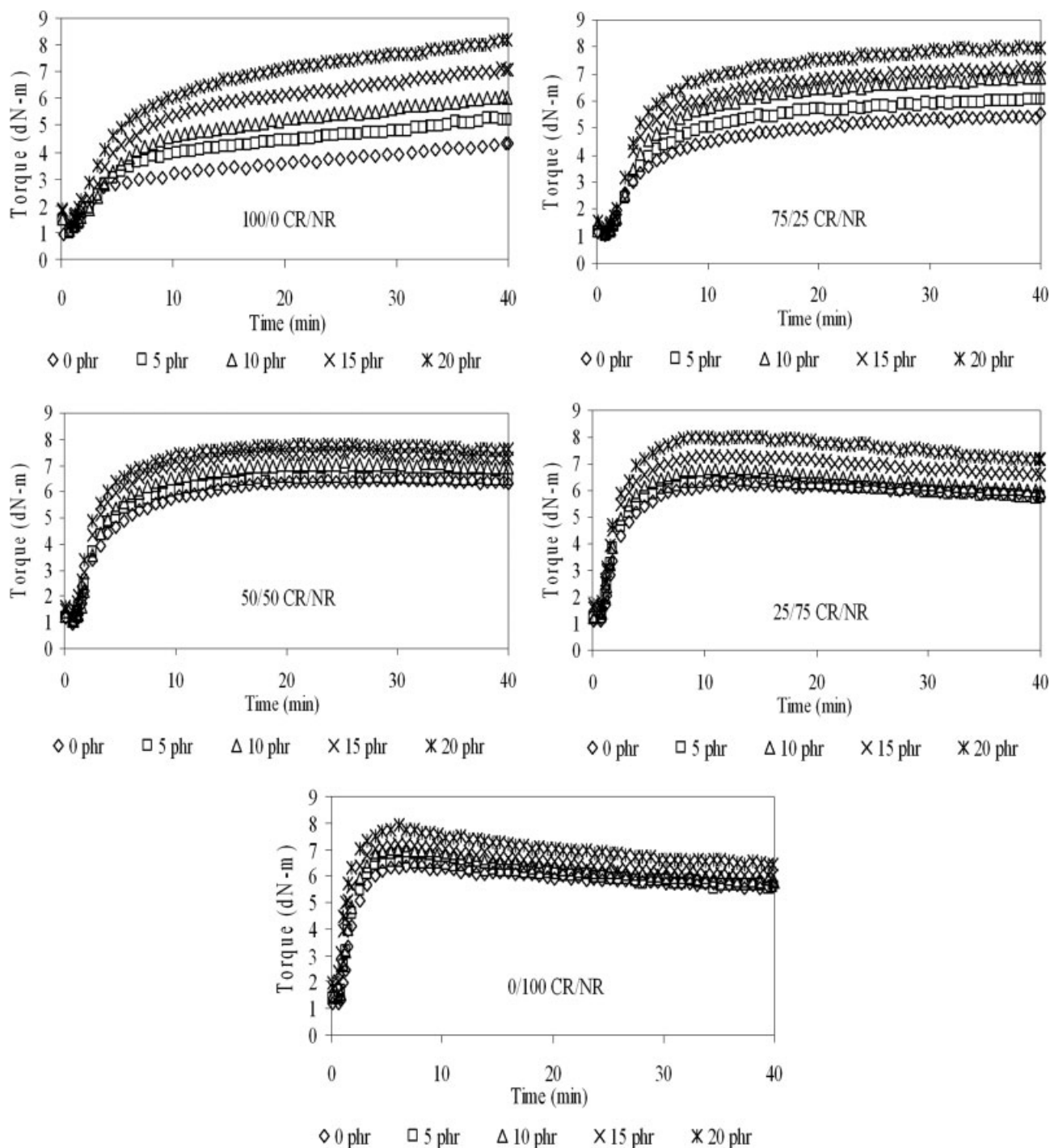
Figure 2 Cure curves of CR, NR, and their blends filled with various $MgCO_3$ loadings.

were obtained for neat NR and the 25/75 CR/NR blend, in which reversion behavior (i.e., a continuous decrease of torque with time after complete cure) was easily observed. However, for the 50/50 CR/NR blend, plateau behavior was observed. This was attributed to the different thermal degradation behaviors of CR and NR. For CR, hydrochloric acid (HCl) gas is evolved from the CR main chain, particularly at high temperatures and long vulcanization times,

which results in the formation of intermolecular crosslinking and/or intramolecular cyclization.[15] This would lead to an indefinite increase of torque during overcuring. Marching behavior or postcuring is, therefore, generally observed in CR. On the other hand, the degradation of NR normally takes place through a chain scission process, which leads to a reduction of both the molecular entanglement and molecular weight and gives rise to the appearance of

Figure 3 Effect of the MgCO$_3$ loading on the marching rate of CR and the 25/75 CR/NR blend.

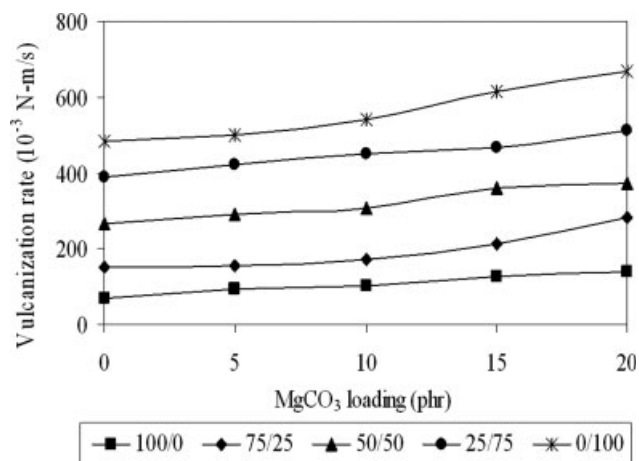**Figure 4** Effect of the MgCO$_3$ loading on the reversion rate of NR and the 25/75 CR/NR blend.

reversion behavior. In addition, reversion in NR also may occur because of the decomposition of the sulfidic linkages and/or the desulfuration, which takes place during vulcanization.[16] This leads to a loss of crosslinks and also to the deterioration of physical properties. Interestingly, we observed that both the marching rate (for CR and the 75/25 CR/NR blend) and reversion rate (for NR and the 25/75 CR/NR blend), as measured from the slope of the curve after complete cure, were dependent on MgCO$_3$ loading. As shown in Figures 3 and 4, both the marching rate and reversion rate tended to increase with increasing MgCO$_3$ loading. The results indicate that MgCO$_3$ could accelerate postcuring in CR. However, for NR, MgCO$_3$ played the opposite role, as it enhanced the degree of reversion. A similar observation was reported previously by Kok.[17] Although the mechanisms of these phenomena have not been clearly elucidated, we proposed that the marching acceleration found in CR was caused by the occurrence of MgCl$_2$, the byproduct of the reaction between MgCO$_3$ and released HCl. Because MgCl$_2$ is a weak Lewis acid, we anticipate that, similar to ZnCl$_2$, MgCl$_2$ was capable of accelerating the dehydrochlorination of CR, which led to the greater degree of marching. For NR, a different mechanism is proposed. As it is widely known that the desulfuration taking place during vulcanization is less when crosslinks are formed more rapidly, with a lower degree of desulfuration, polysulfidic linkages are prone to take place, which will give rise to more opportunities for the thermal decomposition of the network (reversion). As a result, the increased reversion with MgCO$_3$ loading is believed to have arisen from the cure promotion ability of MgCO$_3$. As MgCO$_3$ is basic in nature (pH $\approx$ 10.4), it would promote the rate of sulfur vulcanization (see also Fig. 5). With shorter curing time, a lower extent of desulfuration took place, which
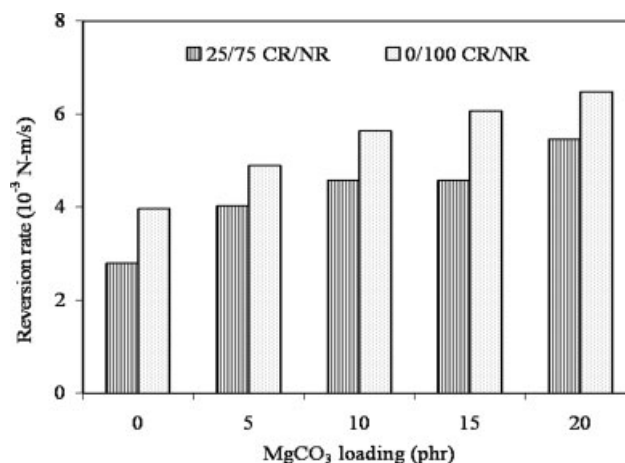
resulted in a reduced proportion of the more stable monosulfidic and disulfidic linkages. The degree of reversion therefore increased with increasing MgCO$_3$ loading.

With regard to the effect of blend ratio on the curing behavior of the blends, we found that, at a given MgCO$_3$ loading, the degree of marching tended to decrease with increasing NR content until a plateau behavior was reached at the 50/50 CR/NR blend ratio, in which the degree of marching in the CR phase and the degree of reversion in the NR phase were counterbalanced. A further increase in NR content resulted in reversion behavior. The dilution effect can be used to explain these results. Figure 5 represents the effect of MgCO$_3$ loading on the vulcanization rate of the rubber compounds. Obviously, for all of the compounds, the vulcanization rate increased continuously with increasing MgCO$_3$ loading. At a given MgCO$_3$ loading, NR possessed the highest vulcanization rate, whereas CR possessed

Figure 5 Effect of the MgCO$_3$ loading on the vulcanization rate of CR, NR, and their blends.
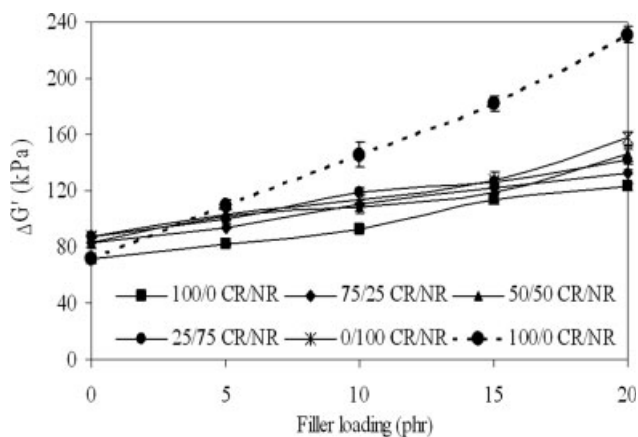
Figure 6 Plot of $\Delta G'$ against the filler loading: (—) $MgCO_3$ and ($\cdots$) SiO_2.

the lowest one. The high vulcanization rate found in NR was attributed to the high reactivity toward the sulfur vulcanization reaction of the double bonds in the NR molecules. Because of the existence of chlorine atoms in the CR molecules, the double bonds in CR were not reactive toward the sulfur vulcanization reaction. CR was, therefore, vulcanized through the use of metal oxides (ZnO/MgO). Despite the addition of an organic accelerator (ETU), the vulcanization rate of CR was still lower than that of NR. For the rubber blends, the vulcanization rate increased with increasing NR content. Again, the results can be explained by the dilution effect.

As shown by the cure curves (Fig. 2), the torque difference (maximum torque−minimum torque) increased with increasing $MgCO_3$ loading. Because it was reported earlier that the torque difference could be used as an indirect indication of the state of cure,[18] the results reveal that $MgCO_3$ could improved significantly the state of cure; that is, the higher the $MgCO_3$ loading was, the greater the state of cure was. It was also easily observed from the cure curves that both the scorch time and optimum cure time of the CR/NR blends tended to decrease with increasing NR content. Again, the results can be explained by the dilution effect because NR was more reactive toward the vulcanization reaction than CR.

Figure 6 represents the relationship between $\Delta G'$ and the $MgCO_3$ loading. Obviously, we found that the $\Delta G'_{unfilled}$ values of all of the compounds obtained in this study were not zero. Although $\Delta G'$ was closely related to the degree of filler–filler interaction, there were many other factors affecting the value of $\Delta G'$, including the entanglement of long-chain molecules. A possible explanation for such finding is, therefore, given by the existence of a gel (pseudocrosslink) in both CR and NR. At low strain, the gel still existed,

which gave rise to a high G'. However, as the strain was increased, the gel could have been partially destroyed, which led to the reduction of G'. $\Delta G'_{unfilled}$ was, therefore, not zero. Because $\Delta G'_{unfilled}$ of NR was greater than that of CR, the results imply that NR possessed a higher gel content than CR. For the $MgCO_3$-filled compounds, $\Delta G'_{filled}$ tended to increase continuously with increasing $MgCO_3$ loading. This was understandable because increasing filler loading resulted in the reduction of the interparticle distance, which gave rise to stronger filler–filler interaction. Although there was evidence of filler–filler interaction, the degree of filler–filler interaction found herein was considered to be very low because, when compared with the results of SiO_2-filled CR (represented by the dotted line in Fig. 6) at a given loading, $\Delta G'$ of the $MgCO_3$-filled compounds was significantly lower than that of the SiO_2-filled compounds. The results clearly indicate that, unlike the highly reactive silica, $MgCO_3$ gave a considerably weaker filler–filler interaction. This might be attributed to the lower interparticle interaction of $MgCO_3$. As the filler loading used in this study was relatively low (≤ 20 phr) and the interaction between $MgCO_3$ particles was relatively weak, the degree of filler–filler interaction found herein was, therefore, not pronounced and could have been negligible.

To confirm the idea that the magnitude of filler–filler interaction was negligible and had no significant effect on the compound properties, the relative elastic modulus at low strain (0.98%), that is, the ratio of G'_{filled} to $G'_{unfilled}$, was plotted against the effective filler volume fraction (ϕ), as shown in Figure 7. The relative elastic modulus calculated from the Guth–Gold equation [eq. (1)] is also plotted in the same figure for comparison:

$$\frac{G'_{filled}}{G'_{unfilled}} = 1 + 2.5\phi + 14.1\phi^2 \qquad (1)$$

Clearly, the relative elastic modulus obtained from the experiment was superimposed well with that calculated from the Guth–Gold equation, particularly at low $MgCO_3$ loadings. Although a slight deviation was observed at high $MgCO_3$ loadings for some compounds, such deviations were very small and insignificant. As it is widely known that the Guth–Gold equation excludes the effects of filler–filler and/or rubber–filler interactions, the results clearly indicate that only a hydrodynamic effect played strong role in G' of the compounds, provided that the loading of $MgCO_3$ was kept below 20 phr.

CONCLUSIONS

In summary, $MgCO_3$ affected the compound viscosity in a similar manner as most other fillers, that is,
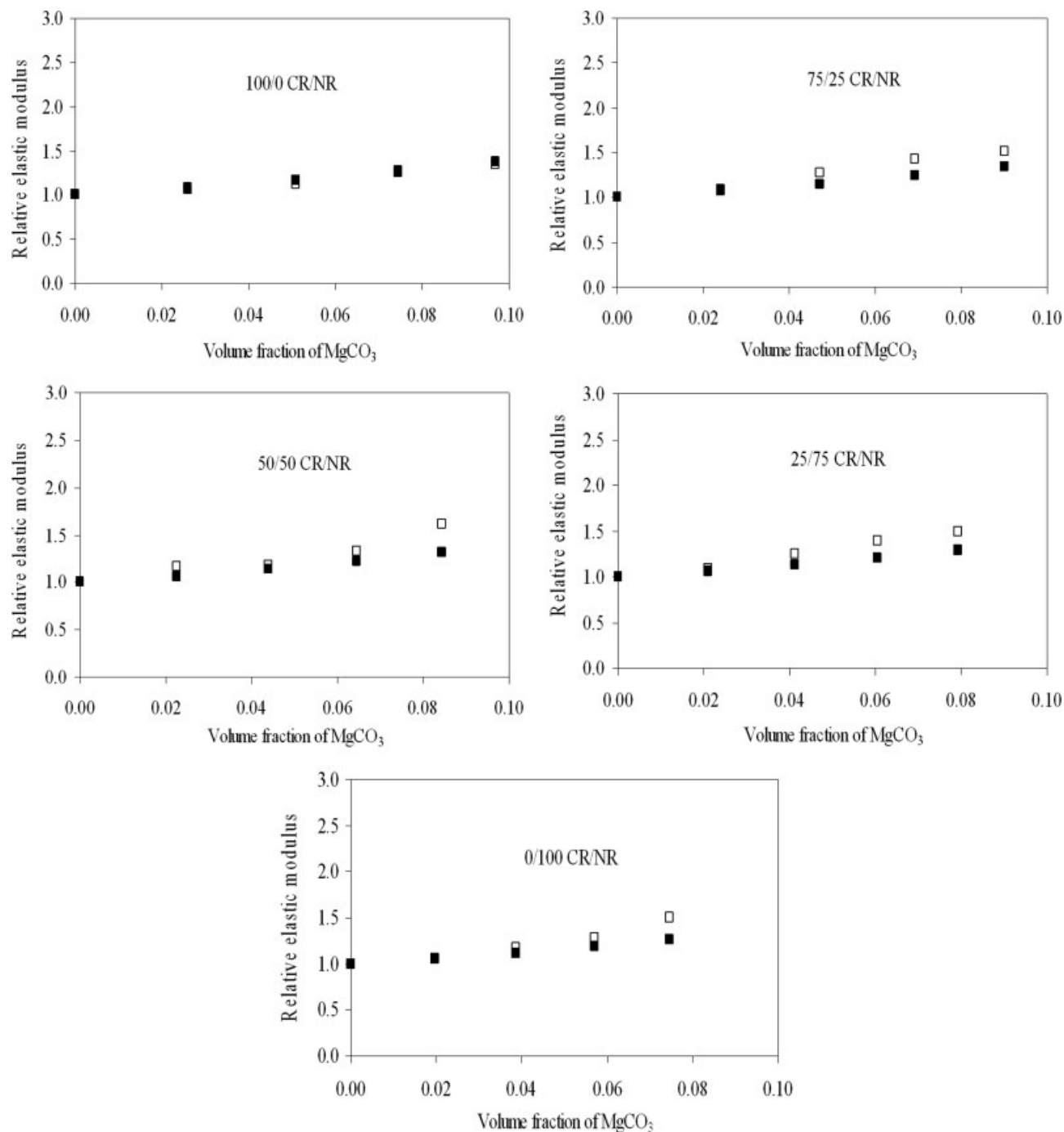
Figure 7 Plots of the relative elastic modulus against the volume fraction of $MgCO_3$ for CR, NR, and their blends: (■) Guth–Gold equation and (□) experimental values.

the higher the $MgCO_3$ loading was, the greater the Mooney viscosity was. At a given $MgCO_3$ loading, the viscosity of the CR/NR blends did not follow the mixture's rule. The negative deviation of viscosity found herein was thought to arise from the high incompatibility of CR and NR. Interestingly, regardless of rubber type, both the vulcanization rate and state of cure were found to increase with increasing $MgCO_3$ loading. However, after complete

cure, $MgCO_3$ influenced the cure characteristics of the rubber compounds differently; that is, it promoted postcuring in CR and promoted reversion in NR. A plateau behavior was observed in the 50/50 CR/NR blend, in which the postcuring and reversion effects were counterbalanced. Although the degree of filler–filler interaction tended to increase slightly with increasing $MgCO_3$ loading, the magnitude of the filler–filler interaction was small and

insignificant. Alternatively, it could be said that, at low $MgCO_3$ loadings ($\leq$20 phr), G' of the compounds was solely controlled by the hydrodynamic effect.

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