MgO and ZnO as Reinforcing Fillers in Cured Polychloroprene Rubber

Yotwadee Chokanandsombat,[1] Chakrit Sirisinha[1,2]

[1]Department of Chemistry, Faculty of Science, Mahidol University, Bangkok 10400, Thailand
[2]Research and Development Centre for Thai Rubber Industry (RDCTRI), Faculty of Science, Mahidol University, Salaya, Nakhon Pathom 73170, Thailand
Correspondence to: C. Sirisinha (E-mail: chakrit.sir@mahidol.ac.th)

ABSTRACT: Polychloroprene rubber (CR) is generally cured in a manner different from that of other diene rubbers. Compounding formulations based on metal oxides have been used satisfactorily for the crosslinking of CR, especially magnesium oxide (MgO) and zinc oxide (ZnO) at loadings of 4 and 5 phr, respectively. In this work, the total loading of MgO and ZnO was varied while the MgO : ZnO loading ratio of 4 : 5 (equivalent to MgO and ZnO volume fractions of 0.013 and 0.009, respectively) that usually used with CR was kept constant. Cure and mechanical properties of CR compounds and cured specimens were investigated. The obtained results could resolve the separate increments in hardness, tensile strength, abrasion resistance, and modulus associated with the increases in crosslink density and total loading of metal oxides. Furthermore, poor compression set and increased heat build-up of cured CR specimens, particularly at high total loading of metal oxides, were believed to be the result of a post-curing effect and of molecular restriction by the increased crosslink density, respectively. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 128: 2533–2540, 2013

INTRODUCTION

Polychloroprene (CR) is an important engineering elastomer widely used in numerous engineering applications. The CR is not characterized by a single property outstanding compared to other elastomers, but does offer an excellent balance of overall properties. In other words, the CR is a general-purpose material having a wide variety of properties, including good mechanical properties, remarkable resistance to hydrocarbon oils, and moderate resistance to most chemicals.[1–4] Furthermore, CR is relatively resistant to flame, ozone, weather, and heat.[1–4] The curing of CR is generally different from that of other diene rubbers.[5,6] This is because the presence of chlorine atoms decreases the reactivity of double bonds on the CR backbone, and thus the reactivity with sulfur. Metal oxide-, thiuram-, and thiourea-based curing agents, particularly ethylene thiourea (ETU), are widely used to cure CR.[7] Recently, newer curing agents, include thiophosphoryl disulfides, dimethyl l-cystine, and cetyltrimethylammonium maleate, have been reported.[8–10] Although there are many published works on various curing agents for CR, the most practical curing agents are still metal oxides due to the superior mechanical properties of the cured products.

It is known that the use of solely zinc oxide (ZnO) generally gives the compounds with relatively poor processing characteristics due to a short premature crosslinking phenomenon (scorch), and the cured specimens with relatively poor mechanical properties.[5] By contrast, the compounds with solely magnesium oxide (MgO) require relatively long cure times, while the crosslink density and mechanical properties of cured specimens are only moderate.[5] With a combination of MgO and ZnO, the cured specimens demonstrate a good balance of mechanical properties and processability.[5,6,11–13] Practically used in the rubber industry, a combination of 4 phr MgO and 5 phr ZnO are commonly selected for crosslinking the CR compounds.[5,6,11]

Although there are many published works reporting the roles of metal oxides on cure characteristics of CR compounds, only a limited number of works focus on the uses of metal oxides as reinforcing fillers. When the CR is compounded with ZnO and/or MgO, the inorganic materials can function both as high-modulus filler and as cure initiator of chain crosslinking reactions. Thus, a point at issue is the relative significance of the catalytic and reinforcing roles of combined MgO and ZnO, compounded with various total loadings. Referred to the metal oxide dosages used in general application of CR, a combination of 4 phr MgO and 5 phr ZnO were used in this work. The MgO to ZnO loading ratio was kept constant while the total loading of MgO and ZnO was varied. In order to fully understand how these metal oxides govern the mechanical properties of the filled CR systems, it is necessary first to resolve the

Table I. Compound Formulations

Ingredient	Density (g/cm^3)	No MO		M4Z5		M8Z10		M12Z15		M16Z20		M20Z25	
		phr[a]	VF[b]	phr[a]	VF[b]	phr[a]	VF[b]	phr[a]	VF[b]	phr[a]	VF[b]	phr[a]	VF[b]
CR	1.23	100	0.840	100	0.822	100	0.805	100	0.788	100	0.772	100	0.756
MgO	3.32	–	–	4	0.013	8	0.025	12	0.036	16	0.047	20	0.058
ZnO	5.57	–	–	5	0.009	10	0.018	15	0.026	20	0.034	25	0.042
ETU	1.27	0.8	0.007	0.8	0.006	0.8	0.006	0.8	0.006	0.8	0.006	0.8	0.006
Sulfur	2.1	0.5	0.002	0.5	0.003	0.5	0.002	0.5	0.002	0.5	0.002	0.5	0.002
Stearic acid	0.85	2	0.024	2	0.024	2	0.023	2	0.023	2	0.022	2	0.022
6-PPD	0.986	2	0.021	2	0.020	2	0.020	2	0.020	2	0.019	2	0.019
DOP	0.986	10	0.105	10	0.103	10	0.101	10	0.099	10	0.097	10	0.095

[a]Part per hundred of rubber. [b]Volume fractions.

relative importance of these two effects (i.e., as high-modulus filler and as cure initiator of chain crosslinking reactions). Since the crosslinking is a rate process, compounding a particular oxide loading for various cure times yields, for further examination, a series of compounds with different crosslink densities but similar filler content. When this is carried out for a variety of oxide contents, the work gives also the samples with similar crosslink density, but different filler volume fractions. Thus, with either contribution kept constant, the two effects can be resolved.

EXPERIMENTAL

Materials
All mixing ingredients were used as-received. CR used in this study was W-type supplied by DuPont Dow Elastomers Co. (Wilmington, DE). Stearic acid and magnesium oxide (MgO) were purchased from Petch Thai Chemical Co. (Bangkok, Thailand). Zinc oxide (ZnO) and sulfur (S_8) were supplied by Chemmin Co. (Samut Prakan, Thailand). N-(1,3-Dimethylbutyl)-N'-phenyl-p-phenylenediamine (6-PPD), as amine-based antioxidant, was supplied by Flexsys Co. (Antwerpen, Belgium). ETU 22S as cure accelerator was produced by Kawaguchi Chemical Industry Co. (Saitama, Japan). Dioctyl phthalate (DOP) as softener was purchased from A.O. Chemical Co. (Bangkok, Thailand).

Preparation of Rubber Compounds
Table I illustrates compounding ingredients used in this work. It must be noted that the ratio of MgO to ZnO of all compounds was kept constant at 4–5, while the total loading of metal oxides was varied progressively. Mixing was performed on two-roll mill (model LRM 150; Labtech Engineering Co., Samutprakarn, Thailand) with a two-stage mixing technique. The roll temperature was set at 50°C. In the first mixing stage, the MgO, stearic acid, 6-PPD, and DOP were incorporated sequentially into raw CR with total mixing time of 17 min. In the second stage, the ZnO, ETU, and sulfur were charged into the rubber mix, and allowed 8 min for achieving good dispersion and distribution of all ingredients.

Preparation of Cured Rubber and Measurement of Cure Characteristics
Cure characteristics, i.e., scorch time (t_{s2}), optimum curing time (t_{c99}), minimum torque (M_L) and maximum torque (M_H) were determined using a moving die rheometer (MDR; Tech-Pro, Ohio) at 155°C. To determine the relationship between storage modulus (G') and crosslink density for various cure times of CR compounds with particular metal oxides loadings, the Rubber Process Analyzer (RPA2000; Alpha technology, Ohio) was used. Referring to Figure 1, the storage modulus (G') at various cure times of CR specimens, incorporating various metal oxides loadings, was measured. Such specimens were thereafter taken for measurement of crosslink density by a swelling technique to be explained in the next section. The arbitrary term "zero crosslink specimen" was defined as the specimen taken from the state at minimum torque (or modulus) as determined from cure curves.
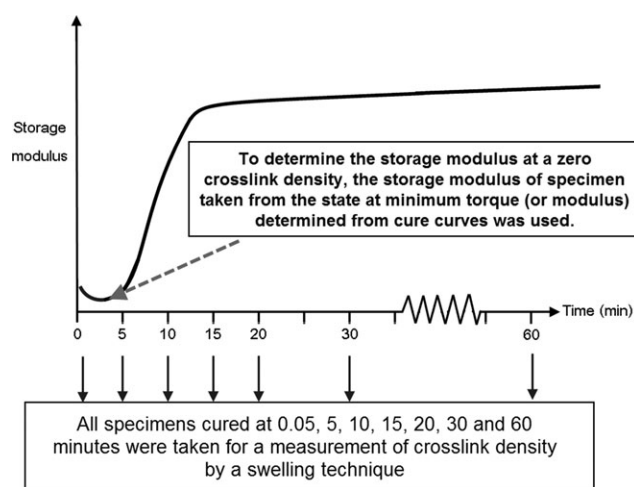

Figure 1. Schematic of the method for determining the relationship between a storage modulus (G') and crosslink density for various cured times of CR compounds with a particular metal oxide loading (as measured by RPA2000 and swelling technique).
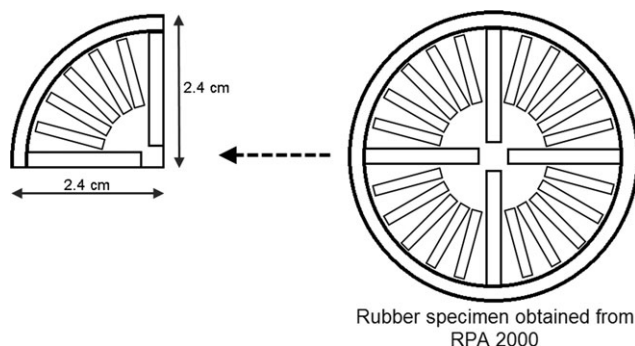
Figure 2. Specimen preparation for a determination of crosslink density via a swelling technique.

Figure 3. Relationship between the storage modulus and the crosslink density of cured CR measured at each set of constant metal oxide filler contents (solid line is used for eye guidance purpose).

To prepare CR cured specimens, the CR compounds were compression molded under a clamping pressure of 12 MPa at 155°C for the optimum cure time (t_{c99}) as pre-determined from the MDR.

Crosslink Density Determination

To determine the relationship between storage modulus (G') and crosslink density of CR cured specimens with particular metal oxides loadings, the cured specimens molded from the RPA2000 were cut into the shape as illustrated in Figure 2. Then the test specimens were weighed, and swollen in toluene for 7 days at room temperature. Thereafter, the swollen specimens were removed from the toluene, and re-weighed. The number average molecular weight between crosslinks, n, was calculated from the Flory–Rehner equation as shown in eq. (1).[14–16]

$$ - [\ln(1 - v_2) + v_2 + \chi v_2^2] = V_1 n \left[v_2^{1/3} - \frac{v_2}{2} \right] \quad (1)$$

where n is the number of elastically active chains per unit volume; V_1 is the molar volume of the solvent; χ is the polymer–solvent interaction parameter (the interaction parameter between CR and toluene = 0.386[11,17]); and v_2 is the volume fraction of polymer in the swollen sample which can be calculated from eq. (2).[16]

$$ v_2 = \frac{m_1 d_s}{m_1(d_s + d_r) + m_2 d_r} \quad (2)$$

where m_1 is the weight of the polymer before swelling, m_2 is the weight of the polymer after swelling, d_s is the density of solvent, and d_r is the density of polymer.

Furthermore, to support the proposed explanation on post-curing effect taking place during the compression set test, the test specimens after the compression set test were taken for determining the crosslink density via the swelling technique, as mentioned previously.

Measurement of Mechanical Properties

Hardness of CR cured specimens was measured using a durometer with Shore A scale (Cogenix Wallace, Surrey) as per ASTM D2240. Tensile properties were determined using a universal testing machine (Instron 5566, Pennsylvania) according to ASTM D412-92 with Die C. Compression set was measured as
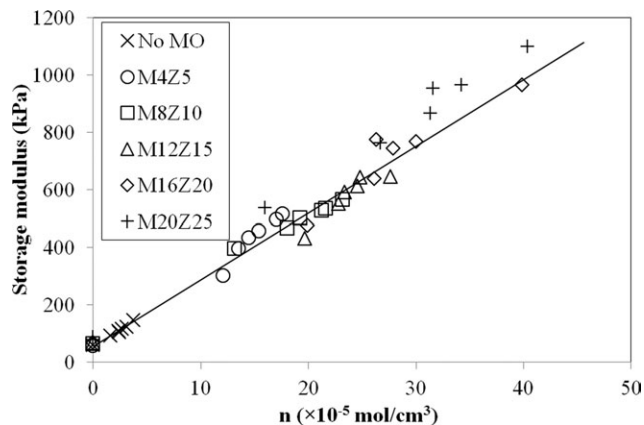
per ASTM D395 method B at 70°C and 100°C for 22 h. To measure the degree of heat dissipation under cyclic deformation, a heat build-up (HBU) test was performed using a HBU flexometer (BF Goodrich Flexometer model II, Ohio) as referred to ASTM D623. It must be noted that the specimens to be measured for the HBU test must include the additional loading of 50 phr N550 carbon black (CB) in order to limit the compressive strain under static loading of 245 N. The DIN-type abrasion device (Zwick Materialprüfung model 6102, Ulm) was used to estimate the relative abrasion resistance of cured specimens, as per ASTM D5963-97. To calculate the abrasion loss, A_A, the loss in mass was converted into volume loss using the determined density of the rubber. After that, the volume loss was corrected by the ratio S_0/S, a characteristic of the abrasive sheet used. Abrasion loss can be calculated using the eq. (3):

$$ A_A = \frac{\Delta m_t \times S_0}{d_t \times S} \quad (3)$$

where A_A is the abrasion loss in mm³, Δm_t is a mass loss of the test specimen in mg, d_t is a density of the test rubber in
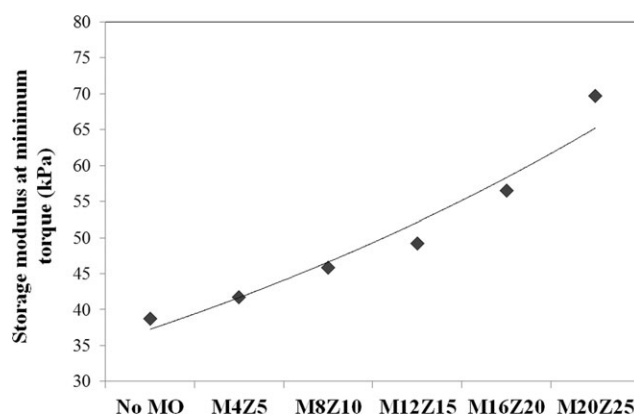

Figure 4. Detail of the storage modulus at zero crosslink density of CR compounds with various total loadings of the filler (solid line is used for eye guidance purpose).
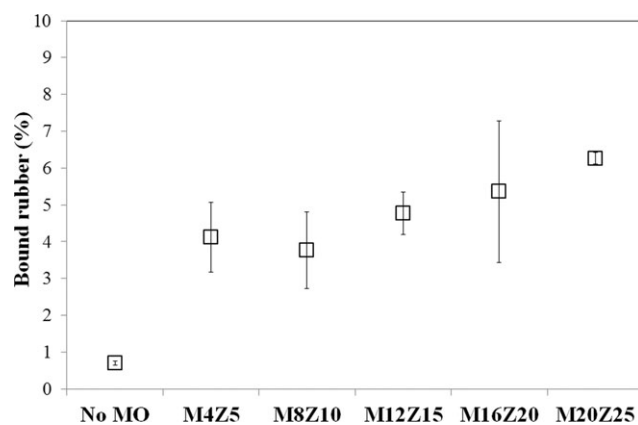
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Figure 5. Bound rubber content of CR compounds at various total metal oxide contents.

Figure 7. Crosslink density (n) of CR cured specimens as determined from the Flory–Rehner equation (○) and torque difference (□) with various total loadings of MgO and ZnO.

mg/mm^3, S_0 is a "normal abrasiveness" of the abrasive sheet (i.e., 200 mg, in this work), and S is the abrasiveness in mg of the abrasive sheet used in the test.

Bound Rubber Measurement

Bound rubber may be a consequence of a high filler–rubber interaction.[18] When compounds of a rubber–filler mixture are extracted with a suitable solvent, then the rubber bound to the filler surfaces may not be penetrated by solvent, and so may not dissolve, although that in the bulk of the compound will go into solution. In this study, the determination of bound, impenetrable (and therefore insoluble) rubber content followed the gravimetric method reported by Wolff el al.[19] Small pieces of ∼ 1 g of uncured specimens were immersed in 80 mL toluene for a total of 7 days at room temperature. After the total 7 days, the bottles containing test specimens with the solvent were filtered out. The residues after extraction were dried in an oven for 1 day at 80°C. The percentages of bound rubber contents can be determined from the following equation.[20,21]

$$\% \text{ Bound rubber content } (\%R_B) = \frac{W_{fg} - W\left[m_f/(m_f + m_p)\right]}{W\left[m_p/(m_f + m_p)\right]} \times 100 \quad (4)$$

where W_{fg} is the weight of filler–rubber gel, W is the weight of the test specimens. The m_f and m_p are the weights of filler and polymer in the rubber compound, respectively.

RESULTS AND DISCUSSION

Cure Characteristics, Rheological Properties, and Bound Rubber Content

Figure 3 represents the relationship between storage modulus, directly measured from the RPA2000, and the crosslink density of CR, as measured from the swelling technique of cured specimens prepared at a set of constant metal oxides contents. It must be noted that, since the specimens taken at the curing time of 0.05 min contained no or very little chemical linkages, most fraction of the rubber matrix is soluble during the swelling measurement. In other words, the calculated crosslink density of these specimens is presumably zero.

The storage modulus increases with increasing crosslink density, most sharply at higher crosslink densities. The variation with filler loading on reinforcement is much smaller than that due to crosslinking. A more detailed picture of the effect of the metal oxides (filler) loading on storage modulus, measured at zero
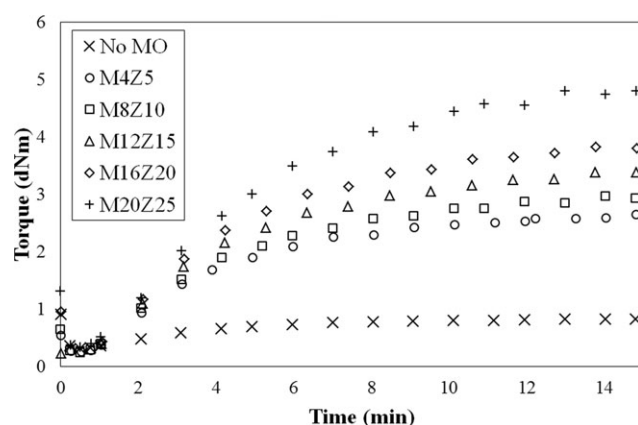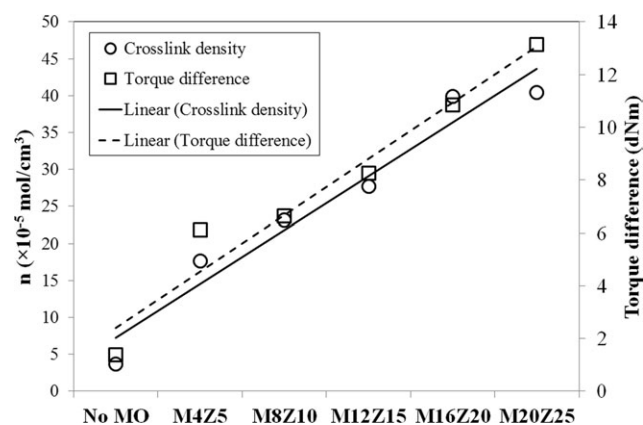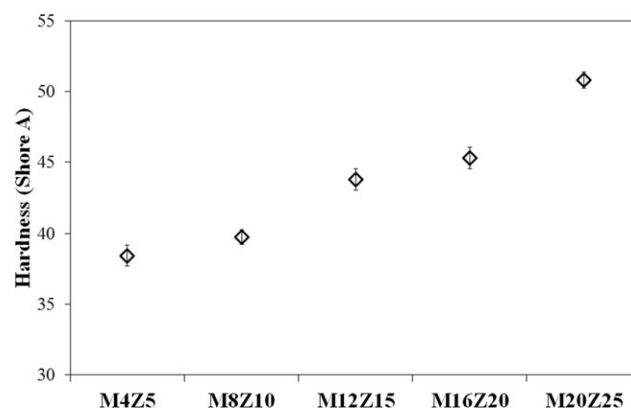

Figure 6. Cure characteristics determined from MDR of CR compounds at various total loadings of metal oxides.

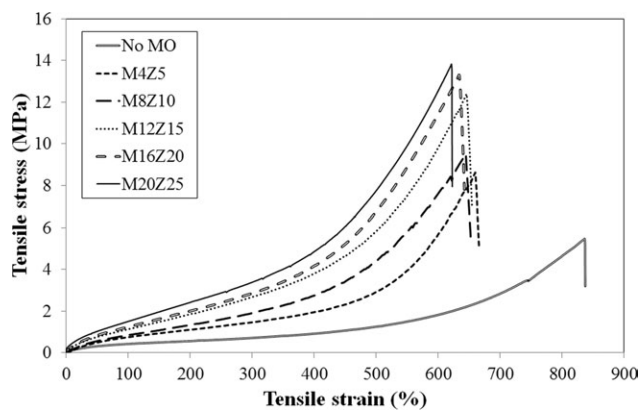**Figure 8.** Hardness of cured CR with various total loadings of MgO and ZnO.

Figure 9. Tensile stress–strain curves of cured CR specimens with various loading of metal oxides.

crosslink density (i.e., the storage modulus determined at minimum torque in cure curve), is shown in Figure 4. Evidently, at this point, the storage modulus increases slightly with increasing metal oxides loading. This, then, is a clear illustration that the magnitude of the reinforcement effect provided by metal oxides with exclusion of any crosslinking is relatively small. In summary, crosslinking is far more important than filler loading in determining the modulus (and related properties) of the cured CR specimens.

Figure 5 shows the plot of % bound rubber content against metal oxides loading. The error bars indicates the standard deviations of the measurements for three specimens in each metal oxides ratio. It is apparent that the total amount of bound rubber increases progressively with the amount of metal oxides. This finding indicates the enhancement in filler–rubber interaction with increasing loading of metal oxides in uncured CR compounds. In other words, the metal oxides behave not only as crosslinking agents, but also as reinforcing filler. Furthermore, referring to Figure 6, the cure characteristics of all CR compounds with various total loadings of metal oxides still reveal the typical "s-shape," i.e., the initial state-of-cure induction period or scorch period, followed by the curing period. This indicates that the CR compounds taken for a measurement
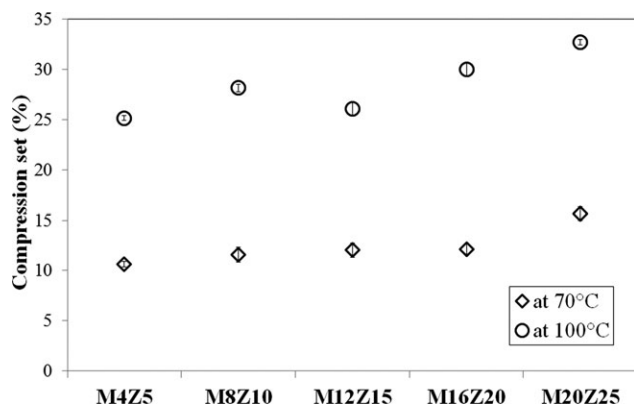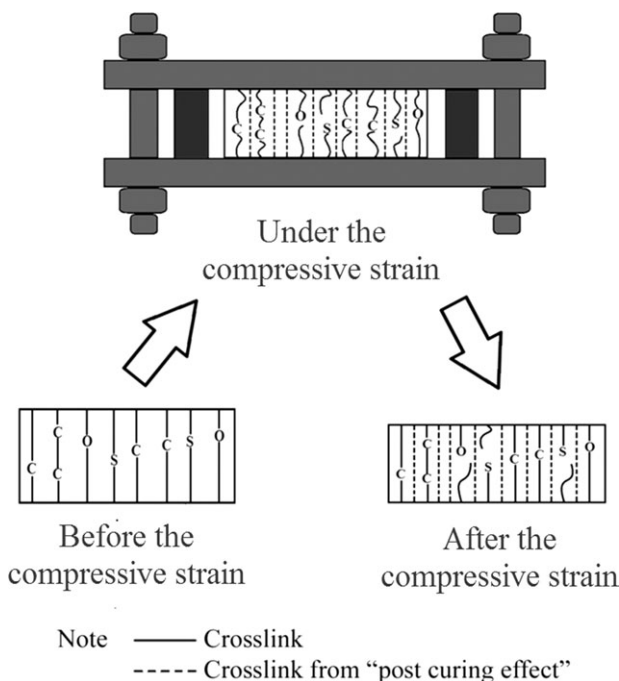

Figure 11. Proposed mechanism of post curing effect on increased compression set.

of bound rubber content contains no significant magnitude of premature crosslink. In other words, the results of bound rubber content as shown in Figure 5 are not interfered significantly by the compound scorch.

It is suggested that the magnitude of the torque difference ($M_H - M_L$) can be used as an indication of crosslink density in rubber cured specimens, i.e., the greater is the torque difference magnitude, the higher is the crosslink density.[22–25] Determination of the crosslink density by the torque difference is confirmed by the comparison shown in Figure 7. The trends of torque difference and crosslink density results are in good accordance suggesting the applicability of torque difference as an indication of crosslink density.

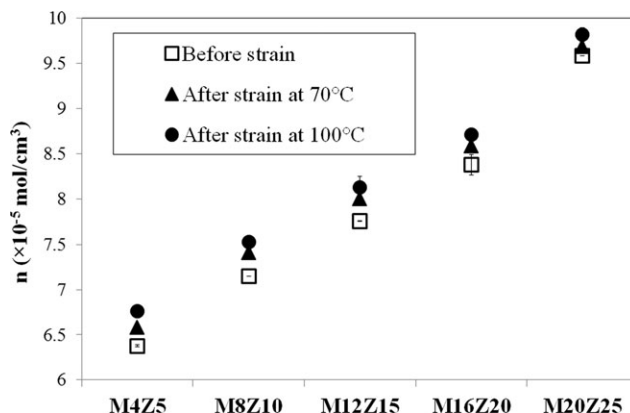**Figure 10.** Compression set at test temperatures of 70°C and 100°C of cured CR with various total loadings of MgO and ZnO.

Figure 12. Crosslink density (n) of compression set test specimens as determined from the Flory–Rehner equation.

Table II. Compression Set Performed at Test Temperatures of 70°C and 100°C of Cured Specimens Prepared with Different State-of-Cure

	Compression set (%)					
	70°C			100°C		
Sample ID	t_{c90}	t_{c99}	t_{c100}	t_{c90}	t_{c99}	t_{c100}
M4Z5	12.78 ± 0.57	10.61 ± 0.28	10.78 ± 0.53	35.56 ± 0.79	25.16 ± 0.22	23.68 ± 0.49
M8Z10	14.47 ± 0.02	11.58 ± 0.76	11.39 ± 0.60	40.91 ± 0.81	28.14 ± 0.36	24.78 ± 0.81
M12Z15	15.33 ± 0.22	12.04 ± 0.71	11.45 ± 0.16	44.18 ± 0.43	26.10 ± 0.63	26.21 ± 0.12
M16Z20	15.54 ± 0.25	12.15 ± 0.49	11.51 ± 0.20	44.46 ± 0.34	30.02 ± 0.63	26.94 ± 0.13
M20Z25	16.65 ± 0.77	15.67 ± 0.68	15.44 ± 0.86	45.80 ± 0.05	32.74 ± 0.27	30.33 ± 0.76

Mechanical Properties

Figure 8 exhibits the variation in hardness with metal oxides loading in CR cured specimens. As expected, the hardness appears to increase slightly, but continuously, with metal oxides total loading. This is attributed to the increased crosslink density in conjunction with a hydrodynamic effect, i.e., the deformable CR matrix is diluted by the rigid metal oxides particles.

Tensile stress–strain curves of cured CR with various metal oxides loadings are shown in Figure 9. The tensile strength tends to increase with increasing metal oxides loading which could be explained by the increased crosslink density of CR specimens. Furthermore, the modulus at 100% strain rises with increased loading of metal oxides which is in line with the results of tensile strength. Generally, the modulus of cured specimens is dependent substantially on the number of crosslink density of rubber specimens.[5] Consequently, such enhanced modulus supports the increment of crosslink density caused by increased total loading of metal oxides.

Figure 10 shows the results of compression set at 70°C and 100°C of cured CR specimens filled with various metal oxides loadings. The compression set at 70°C appears to increase slightly with increasing metal oxides loading. At a test temperature of 100°C, the sensitivity of compression set to metal oxides loading is more obvious. These compression set results are not in line with the usual interpretation of the crosslink density results stated above. Generally, and in contrast to these observations,

with increasing crosslink density the elastic contribution should increase and thus compression set should decrease. An explanation of these unexpected compression set results is proposed in terms of a "post-curing effect." As mentioned elsewhere, the CR can be crosslinked in the absence of a curing agent, particularly at high temperatures.[5] It is, therefore, highly susceptible to a post-curing phenomenon.[15,26] In this work, it is believed that the post-curing effect taken place under the compressive strain is caused by the split of non-flexible bonds accompanied with the formation of new bonds, as shown in Figure 11. As a consequence, after load removal, the crosslinks formed under compressive strain restricts the elastic recovery of the test specimens. This, in turn, leads to the increase in final compression set.

In order to support the proposed explanation, the measurement of crosslink density via swelling test on test specimens before and after compressive strain was conducted, and the results obtained are exhibited in Figure 12. Evidently, the test specimens after being compressed at the temperature of 70°C show greater crosslink density than that prior to being compressed. This finding is even more pronounced in the specimens being compressed at high temperature of 100°C. Such increase in crosslink density supports the occurrence of post-curing effect during the compression set test as discussed previously.

To monitor the state-of-cure effect on compression set, the cured CR specimens were prepared with different cure times to produce the cured products with different state-of-cure. As illustrated in Table II, cure times of t_{c90}, t_{c99}, and t_{c100} would
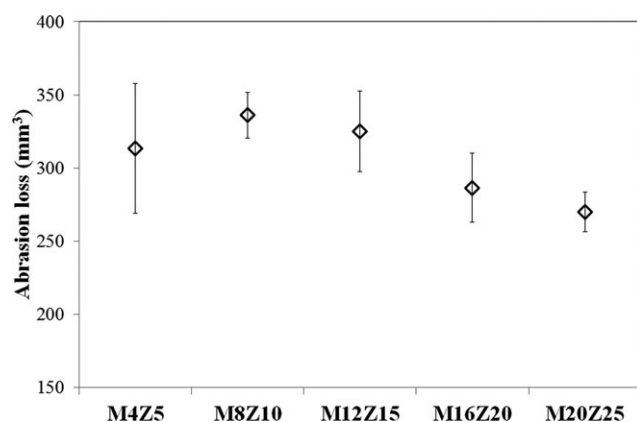
Figure 13. Abrasion loss of cured CR with various total loadings of MgO and ZnO.
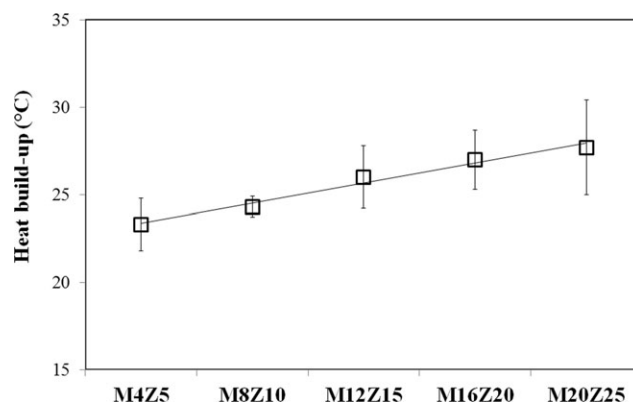
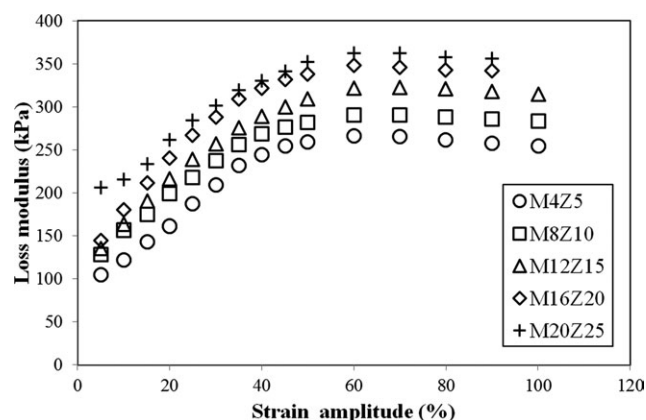**Figure 14.** HBU of cured CR with various total loadings of MgO and ZnO.

Figure 15. Loss modulus (G'') as a function of % strain at frequency of 5 rad/s in CR compounds with increasing total loading of MgO and ZnO in CB systems.

offer the cured product having state-of-cure of 90%, 99%, and 100% of complete cure, respectively. It is apparent that all CR specimens still show the post-curing effect, but the magnitude of such effect tends to decrease with increasing state-of-cure. The results are strong evidences supporting the occurrence of post-curing effect during the compressive strain as discussed earlier.

The relationship of abrasion loss of cured CR and metal oxides loading is shown in Figure 13. Clearly, the abrasion loss tends to decrease slightly with metal oxides loading. It is known that the abrasion resistance of rubber is complex, and involves with more than one mechanism.[27] Factors governing the abrasion resistance of cured rubber specimens include crosslink density, hardness, modulus, and friction coefficient.[28,29] The greater crosslink density and, hence, the hardness and modulus give rise to the improvement of abrasion resistance.[28] As a result, the enhancement in abrasion resistance with increasing metal oxides loading is explained by the increased magnitudes of crosslink density and filler reinforcement.

HBU of cured CR specimens is exhibited in Figure 14. It is apparent that the HBU is dependent on metal oxides loading, and unexpectedly increases with increasing total loading of metal oxides. Initially, it is anticipated that the rise in crosslink density caused by the increased metal oxides loading will reduce the energy dissipation per cycle, and thus the HBU. The explanation of observation is postulated by the greater restriction of molecular chain flexibility caused by the higher crosslink density leading to an increase in the energy required to create free volume and thus the greater magnitude of hysteresis process.[30] Similar findings are reported in tightly-crosslinked materials including resin-cured elastomers.[31] Also, referring to Figure 15, the increase in loss modulus (G'') is found to increase with total loading of metal oxides, supporting the proposed explanation of increased HBU as a result of chain motion restriction.

CONCLUSIONS

The specimens of CR, cured at various cure times, and incorporating various total loadings of MgO and ZnO, were prepared

and measured for their properties. Changes in crosslink density were monitored, and correlated with the modulus. By keeping the MgO to ZnO loading ratio at 4 : 5, the crosslink density of cured specimens (as determined from swelling techniques) increases significantly with increased total loading of metal oxides. Furthermore, the storage modulus increases linearly with increasing crosslink density. The storage modulus could be enhanced by increased crosslink density more effectively than the filler reinforcement effect.

Results of hardness, tensile properties, and abrasion resistance agree well with those of crosslink density. Unexpectedly, despite the increase in crosslink density, poor compression set is observed, due probably to the post-curing effect. The HBU increases with increasing total loading of metal oxides, which might be caused by increased restriction of chain internal rotation as a result of the increased crosslink density.

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