A New Method to Predict Optimum Cure Time of Rubber Compound Using Dynamic Mechanical Analysis

S. Raa Khimi, K. L. Pickering

School of Engineering, The University of Waikato, Hamilton 3216, New Zealand
Correspondence to: K.L. Pickering (E-mail: klp@waikato.ac.nz)

ABSTRACT: The degree of vulcanization of a rubber compound has a big influence on the properties of the final product. Therefore, precisely defining the curing process including optimum cure time is important to ensure the production of final products having high performance. Typically, vulcanization is represented using vulcanization curves. The main types of equipment used for producing vulcanization curves are the oscillating disc rheometer (ODR) and the moving die rheometer (MDR). These can be used to plot graphs of torque versus time at a constant temperature to show how cure is proceeding. Based on the results obtained, optimum cure time (t_{90}) is calculated as the time required for the torque to reach 90% of the maximum achievable torque. In this study, the use of Dynamic Mechanical Analysis (DMA) for assessment of t_{90} was assessed. DMA was carried out using shear mode isothermal tests to measure the changes in material properties caused by vulcanization. The results revealed that the shear storage modulus (G'), shear loss modulus (G''), and tan δ all reflect the vulcanization process, however, tan δ gave the best representation of level of vulcanization. Indeed, the curve of tan δ was able to be used to derive the t_{90} for rubber compounds and showed good agreement with the results from an MDR. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40008.

INTRODUCTION

Rubbers are one of the most widely used groups of materials in engineering products. The advantages of rubbers such as elasticity and high damping make them dominant in various applications including tires, dampers, gaskets, seals, and conveyor belts. However, in order to produce its unique material properties, the rubber compound, which is generally a mixture of rubber, vulcanization agent, accelerator, fillers, and several additional ingredients, needs to be vulcanized to form a cohesive rubber based solid. During the vulcanization process, the rubber compound is heated up to a temperature at which irreversible reaction between the rubber molecular chains and the vulcanization agent starts to form crosslinks leading to an elastic, three-dimensional structure.[1]

Typically, vulcanization is represented using vulcanization curves such as that shown in Figure 1. The main types of equipment used for producing vulcanization curves are the oscillating disk rheometer (ODR) and the moving die rheometer (MDR), both of which are technically classified as curemeters.[2–4] In a curemeter, a piece of rubber compound is contained in a sealed test cavity with a rotor that oscillated at a constant angular displacement. As vulcanization proceeds at a specific temperature, the torque required to shear the compound is monitored and a

curve of torque versus time can be generated.[4,5] The working principal of the curemeter is based on the fact that the stiffness of the rubber compound increases with the formation of the crosslinks during vulcanization. The use of a curemeter to determine the vulcanization characteristics is specified in ASTM D 2084.[6]

Generally, three stages are clearly represented by a vulcanization curve. The first stage is the induction period which is characterized by slow chemical reaction between rubber and the additives. It enables safe processing and good flow of the rubber compound inside a mould cavity. The second stage is where curing of rubber molecular chains occur to form network structures. Vulcanization rate can be considered as the rate of this stage. Optimum cure time (t_{90}), which as stated earlier, is the time required for the torque to reach 90% of the maximum achievable torque (T_{90}) and relates to the time necessary for the cured rubber to achieve optimal properties.[7] The last stage can involve overcuring reactions depending on the rubber type, vulcanization agent and temperature. In an ideal case, an equilibrium degree of vulcanization is obtained and the torque versus time graph plateaus. However, some compounds show reversion due to overheating during the test that corresponds to break down of rubber networks. Conversely, additional crosslinks may
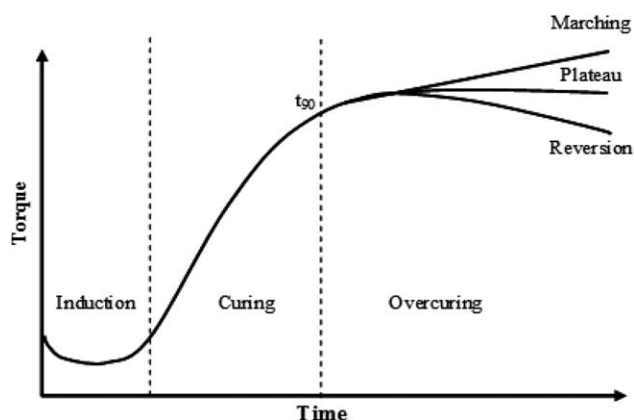
Figure 1. Vulcanization curve of rubber.

occur (induced by reaction of very reactive vulcanization agent such as hyperoxides) to produce a marching curve. It is well known that overcure of rubber compound usually has an undesirable effect on product quality. Therefore, a precise determination of cure time is necessary to ensure the production of final products having optimum performance with competitive cost.[4,5,8]

In addition, a good understanding of factors that affect vulcanization is crucial to predict the optimum cure time. Rubber

compounds that have different formulations may not produce the same network density. Some of the most important factors that affect the cure time are addition of fillers, formation of sulphur linkages, and thermal instability of sulphur linkages.[2,3] The effect of cure time is more evident in the compound with filler due to rubber–filler interactions.[9] For filled elastomers, the cure time is usually shorter than unfilled elastomers and the maximum torque value increases as filler content increases.

Considering the fact that the fundamentals of curemeter application involve monitoring the shear modulus to assess the vulcanization, suggest that the shear mode of Dynamic Mechanical Analysis (DMA) could also be used for evaluating the optimum cure time of a rubber compound. DMA can be simply described as applying a sinusoidal deformation to a sample whilst analyzing the material's response to that deformation. From this, a variety of fundamental material parameters can be determined such as storage and loss modulus, tan δ, viscosity, and glass transition temperature. Lately, DMA has been used for monitoring cure of thermosetting resins, by which the viscosity of the initial stage of curing and the latter stage of curing (after gelation) are generally studied. Based on the changes in viscosity, DMA can detect cure development and important transitions in cure process such as gelation and vitrification point.[10–13] However, according to the author's knowledge, no comprehensive work was dedicated to monitor and predict optimum cure time

Table I. Formulations of Rubber Compound

Material	Natural rubber	ZnO	Stearic Acid	CBS	TMTD	Paraffin oil	Naphthenic oil	Sulphur	Titanomagnetite loading	Titanomagnetite particle size
Sample/Unit	phr	phr	phr	phr	phr	phr	phr	phr	phr	μm
1	100	5	1	2	1	2	3	1.5	0	0
2	100	5	1	2	1	2	3	1.5	30	0–32
3	100	5	1	2	1	2	3	1.5	30	32–45
4	100	5	1	2	1	2	3	1.5	30	45–56
5	100	5	1	2	1	2	3	1.5	30	56–75
6	100	5	1	2	1	2	3	1.5	30	75–106
7	100	5	1	2	1	2	3	1.5	50	0–32
8	100	5	1	2	1	2	3	1.5	50	32–45
9	100	5	1	2	1	2	3	1.5	50	45–56
10	100	5	1	2	1	2	3	1.5	50	56–75
11	100	5	1	2	1	2	3	1.5	50	75–106
12	100	5	1	2	1	2	3	1.5	70	0–32
13	100	5	1	2	1	2	3	1.5	70	32–45
14	100	5	1	2	1	2	3	1.5	70	45–56
15	100	5	1	2	1	2	3	1.5	70	56–75
16	100	5	1	2	1	2	3	1.5	70	75–106
17	100	5	1	2	1	2	3	1.5	100	0–32
18	100	5	1	2	1	2	3	1.5	100	32–45
19	100	5	1	2	1	2	3	1.5	100	45–56
20	100	5	1	2	1	2	3	1.5	100	56–75
21	100	5	1	2	1	2	3	1.5	100	75–106
phr, per hundred rubber										

Table II. Optimum Cure Time (t_{90}) of the Formulations as Evaluated by MDR

Sample	t_{90} MDR (min)
1	5.10
2	4.65
3	5.19
4	4.85
5	5.25
6	4.71
7	4.41
8	4.82
9	4.64
10	4.51
11	4.92
12	4.46
13	4.42
14	4.58
15	4.31
16	4.47
17	4.47
18	4.70
19	4.55
20	4.54
21	4.20

of rubber compounds. In this study, the DMA is tested for suitability for monitoring cure of rubber compounds.

EXPERIMENTAL

Material and Specimen Preparation

In order to check the applicability of DMA to predict the optimum cure time and to evaluate the consistency of the measurements, 21 formulations of rubber compound were investigated. The formulations used in this study are shown in Table I. Natural rubber (SMR L) and other chemicals such as zinc oxide, stearic acid, *n*-cyclohexyl-2-benzothiazole sulfenamide (CBS), tetra methyl thiuramdisulphide (TMTD), paraffin oil, and

naphthenic oil were all purchased from Field Rubber Limited, Auckland. Both unfilled and filled rubbers were involved in this study. Titanomagnetite was used as filler, which was milling to various sizes using planetary mono mill (Pulverisette 6) produced by Fristech GmbH.

The mixing and compounding was carried out using a conventional laboratory two roll mill (model XK150) according to ASTM designation D3184-80. Nip gap (distance between front and back roller), time of compounding and sequence of addition of the ingredients (the ingredients were added in the following sequence: rubber, activator, plasticizer, filler, accelerator, and crosslinking agent) were kept constant for all the compounds. Samples were punched from the uncured compound in the form of circular discs with 10 mm diameter and thickness of 3 mm for DMA shear mode testing.

Equipment and Procedure

Moving Die Rheometer (MDR). The MDR 2000 is a rotor less curemeter designed to measure vulcanization of rubber compounds under isothermal test conditions with constant strain and frequency. It has gained much acceptance by the rubber industry and offers several substantial advantages over previous ODR techniques as described in ASTM D 2084. The design of the MDR 2000 allows the lower half of the die to perform an oscillating rotation of 0.5° with torque measured at the upper die by a torque transducer. The curing characteristics of the compound were determined at 150°C under a constant frequency of 1.66 Hz and the t_{90} values were derived from the vulcanization curve. The results of the cure time measurements with the MDR are listed in Table II.

Dynamic Mechanical Analysis (DMA). The DMA instrument used to perform these experiments was a Perkin Elmer DMA 8000. It is made up of six major components (Figure 2): a force motor, a drive shaft, a high sensitivity displacement detector (LVDT), a sample fixture, a furnace, and a temperature controller. DMA measurements were conducted on circular disc specimens in shear mode. The specimen loading is shown in Figure 3. The driveshaft motion was kept in a horizontal direction during the test and the temperature controller was placed at a minimum distance from the sample. The furnace was first preheated to 150°C and then an isothermal test was carried out
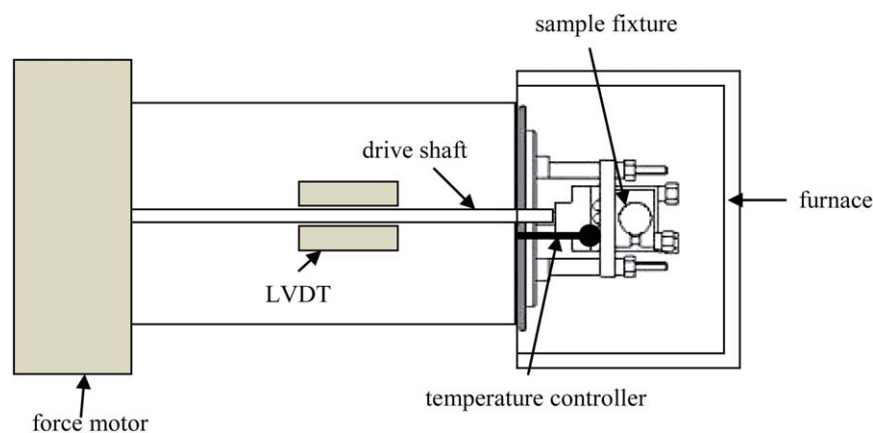
Figure 2. Scheme of the DMA 8000. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
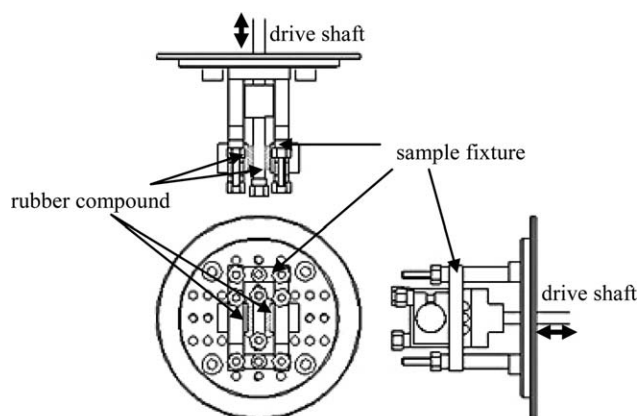
Figure 3. Scheme of the shear mode specimen loading in DMA.

under a fixed frequency of 1.66 Hz and constant displacement amplitude of 0.1 mm. The temperature was held at 150°C for 15 min to allow full vulcanization to occur. Data were collected approximately every 5 s in the isotherm period. Shear storage modulus (G'), shear loss modulus (G'') and tan δ were recorded as a function of time in order to deduce a direct connection between the dynamic time sweep test and optimum curing time.

RESULTS AND DISCUSSION

A typical time sweep plot of the unfilled natural rubber compound (NR) measured by DMA is shown in Figure 4, including G' and G''. As can be seen, G' increases representing when the curing process started and reaches a peak after 5 min. This is thought to be due to softening of the material as the material is exposed to the oven temperature. After the maximum point, G'' was found to decrease rapidly for 3 min, followed by a gradual decrease for approximately 15 min. This is believed to occur due to the reduction of viscous flow in the material and therefore low energy being absorbed. In contrast, it is apparent that G' does not change at the beginning of the curing stage. This indicates that the stiffness of the rubber remains low at the early stage of vulcanization. After 5 min, a rapid increase of G' was observed, followed by a continuous increment up to 15 min. This represents the increase of stiffness as a result of crosslink formation. The results obtained agreed with previous work carried out by Gatos et al.[14] using a plate–plate rheometer.
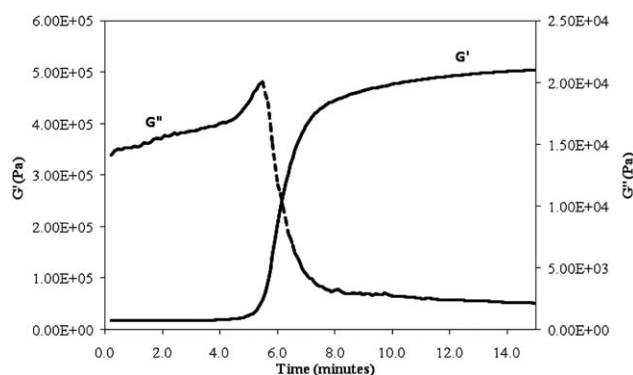
Table III. Differences of t_{90} Value Measured by MDR and Calculated from the Gelation Point of G'' or G' Graphs for Unfilled Natural Rubber Compound (NR)

Method		Time
	t_{90} MDR	5.1 min
	t_{90} Gelation Point	6.1 min
Error (%)		20%

Altogether, it can be seen that neither parameter shows a plateau value that indicates an equilibrium degree of vulcanization. A gelation point can be detected at 6.1 min; the gelation point is taken to be the crossover of G'' and G' where tan δ equals 1. In monitoring cure of thermosetting resins by DMA, the gelation point can be defined as a point where the crosslinks have progressed to form a network across the specimen and the material changes from a viscous liquid to a viscoelastic solid.[15] However, the values obtained show a significant difference with the value from a conventional curemeter with an average percentage error of 20% (Table III). It can be concluded that there is not a direct correlation between t_{90} and G'' or G' graphs.

Another important parameter obtained in dynamic time sweep test is tan δ. Tan δ is calculated as the quotient of the loss and the storage moduli. Therefore, it reveals the ratio of the viscous and the elastic portion of the materials.[16] The results for tan δ as a function of time for NR are depicted in Figure 5. As can be seen, three stages of curing process can be observed for the tan δ curve suggests that, this parameter and its changes with time apparently reflect the development of crosslinking reaction inside the rubber. In induction period, tan δ increased to a maximum which indicates the softening of the material and slow chemical reaction between vulcanizing agent, rubber and other compound constituents. The peak could relate to where optimum flow of the rubber compound through the mould cavity can occur giving the compound its final shape for curing. In the curing stage, tan δ was found to decrease rapidly which can again be explained by development of crosslinks between the rubber molecular chains that increase the elasticity of the
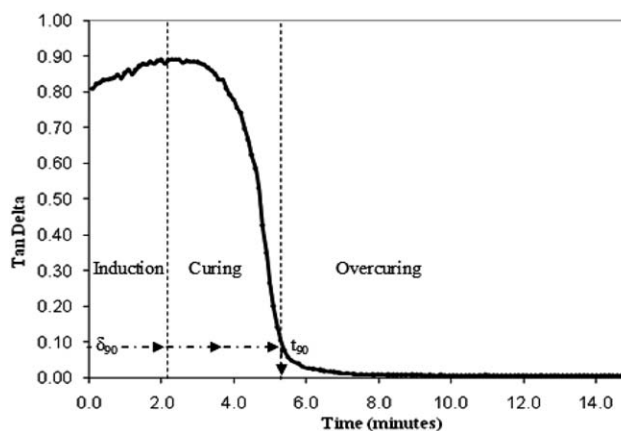

Figure 4. Time sweep plot, including G'' and G' for NR compound.

Figure 5. Tan δ curve as a function of time for NR compound.

Table IV. Percentage Error of Optimum Cure Time (t_{90}) Measured by DMA

Sample	t_{90} MDR (min)	t_{90} DMA (min)	DMA error (%)
1	5.10	5.30	3.92
2	4.65	4.70	1.08
3	5.19	5.10	−1.73
4	4.85	4.80	−1.03
5	5.25	5.40	2.86
6	4.71	4.50	−4.46
7	4.41	4.30	−2.49
8	4.82	4.70	−2.49
9	4.64	4.50	−3.02
10	4.51	4.60	2.00
11	4.92	4.80	−2.44
12	4.46	4.50	0.90
13	4.42	4.20	−4.98
14	4.58	4.50	−1.75
15	4.31	4.20	−2.55
16	4.47	4.50	0.67
17	4.47	4.60	2.91
18	4.70	4.90	4.26
19	4.55	4.60	1.10
20	4.54	4.60	1.32
21	4.20	4.40	4.76
Average error (%)			0.58

material. As previously discussed, the end of this stage corresponds to the optimum vulcanization time (t_{90}). In most cases of torque versus time graphs (vulcanization curves) generated by the MDR, the final stage of vulcanization is characterized by a plateau at a maximum value.[14] A potentially equivalent plateau is well resolvable in the tan δ curve, but tan δ stabilizes at a minimum value as a function of time.

In a typical MDR vulcanization curve, the time to achieve the optimum network density, at a given temperature is the time required for the torque to reach 90% of the maximum achievable torque.[6] The T_{90} can be calculated as follows:

$$T_{90} = T_{min} + 0.9 (T_{max} - T_{min}) \tag{1}$$

where T_{max} and T_{min} are the maximum and minimum torque values. The value of t_{90} can now be found from the graph of torque versus time. Considering the capability of the DMA to monitor the formation of the crosslinking network by the tan δ curve, an equivalent t_{90} could be obtained similiarly from δ_{90} according to Eq. (2):

$$\delta_{90} = \delta_{max} - 0.9(\delta_{max} - \delta_{min}) \tag{2}$$

where now δ_{max} and δ_{min} are the maximum and minimum tan δ values. It is assumed that t_{90} could now be obtained from tan δ versus time graphs at δ_{90}. From the tan δ curve of NR in

Figure 5, the t_{90} value obtained using Eq. (2) is 5.3 min. There was little difference between MDR and DMA values with percentage error of 3.9%. It should be mentioned at this point that even different types of conventional curemeters present variation of optimum curing time for the same sample.[14] Therefore, as both techniques use a shear excitation and measure a quantity that is related to the shear modulus, the similarity is reasonable.

In addition, it is possible that cure rate could also be determined from the tan δ versus time curve, as a decrease in tan δ value with time such that it could be obtained by the slope in the curing stage. However, further work would be needed to assess that. The sensitivity of the DMA is also sufficient to record the overcuring of rubber (after t_{90}).

In order to assess that DMA is reliable for assessment of t_{90}, further rubber compounds were analysed. In this step, t_{90} of 20 further rubber compounds with various filler loading and particle size as mentioned in Table I were measured using MDR and DMA. A percentage error criteria was used for comparison of these two techniques. The percentage errors for t_{90} measurements using DMA are given in Table IV. In view of the results obtained, the percentage errors for all compounds were lower than +/− 5% with average percentage error of 0.58%. The results for all compounds at different particle sizes and loading were satisfactory and reliable with acceptable proximity. This indicates that the DMA is capable to measure different types of curing behaviours which is more apparent in the compounds with fillers as discussed ealier.

CONCLUSIONS

This study was devoted to assess the capability of DMA to predict the optimum curing time (t_{90}) of rubber compounds. This was performed by investigating natural rubber compounds with a conventional sulphur crosslinking system. It is known that the oscillating disk rheometer (ODR) and moving die rheometer (MDR) are by far the most commonly used equipment to characterize the curing behavior of rubbers. The results of isothermal curing test of the DMA indicate that several parameters such as shear storage modulus (G'), shear loss modulus (G'') and tan δ reflect the vulcanization process. However, only the tan δ curve shows a strong correlation with crosslink development. This means that the three stages of curing can be clearly observed, with the final stage of vulcanization characterized by a plateau. Contradictory to the typical MDR vulcanization curve where the torque reaches maximum, tan δ value stabilizes at a minimum value and the t_{90} can be calculated as the time when tan δ reduces to 90% of its maximum value. The measured values were generally in agreement with results obtained by a MDR with range of errors lower than +/− 5% and average percentage error of 0.58%. Overall, the presented results show that DMA can be use as a new equipment to predict the optimum curing time of rubber.

ACKNOWLEDGMENTS

REFERENCES

1. Jaunich, M.; Stark, W.; Hoster, B. *Polym. Test.* **2009**, *28*, 84.

2. Deniz, V.; Karaagac, B.; Inal, M. *Mater. Design* **2008**, *35*, 833.

3. Deniz, V.; Karaagac, B.; Inal, M. *Mater. Design* **2009**, *30*, 1685.

4. Ciesielski, A. *An Introduction to Rubber Technology, Vol. 1*; Rapra Technology Limited: Shawbury, Shrewsbury, Shropshire, SY4 4NR, UK, **1999**. p 1.

5. Hoffman, W. *Rubber Technology Handbook*; Hanser/Gardner Publications: Cincinnati, **1989**. p 475.

6. ASTM-D2084, Standard Test Method for Rubber Property—Vulcanization Using Oscillating Disk Cure Meter. ASTM International: West Conshohocken, **2011**. p 11.

7. Simpson, R. B. *Rubber Basics*. Rapra Technology: Shawbury, UK, **2002**. p 212.

8. Aggarwal, S. L. *J. Polym. Sci. Part C: Polym. Lett.* **1990**, *28*, 210.

9. Leblanc, J. L. *Prog. Polym. Sci.* **2002**, *27*, 627.

10. Stark, W. *Polym. Test.* **2013**, *32*, 231.

11. Tsang, C. F.; Hui, H. K. *Thermochim. Acta* **2001**, 367–368, 169.

12. Wang, J.; Laborie, M.-P. G.; Wolcott, M. P. *Thermochim. Acta* **2007**, *465*, 18.

13. Xie, M.; Zhang, Z.; Gu, Y.; Li, M.; Su, Y. *Thermochim. Acta* **2009**, *487*, 8.

14. Gatos, K. G.; Karger-Kocsis, J. *Kautschuk Gummi Kunststoffe* **2004**, *57*, 350.

15. Menard K. P. Time and Temperature Scans Part II, in Dynamic Mechanical Analysis; CRC Press: Boca Raton, **2008**. pp 123–143.

16. Mezger, T.G. The Rheology Handbook, 2 ed.; Curt R. Vincentz: Hannover, Germany, **2006**. p 299.