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Enthalpy profile-cure state relationship of compounded rubber by differential scanning calorimetry

Kyo-Chang Choi, Eun-Kyoung Lee*,†, and Sei-Young Choi***

*Department of Applied Chemistry, Cheongju University, Cheongju 360-764, Korea
**Strategy Planning Team/Bio Development Team Meta Biomed, 1115-6, Cheongwongun, Choongbuk 363-911, Korea

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Abstract−Differential scanning calorimetry (DSC) was applied to natural rubber (NR) and NR/recycled natural rubber (RNR)(NR/RNR) blend to understand and optimize the state of cure, which is based on the value of the exothermic reaction obtained in process of vulcanization. Swelling and mechanical data were investigated with the increase of cure time from 15 to 35 minutes with an interval of 5 minutes and compared with the DSC enthalpy data. With the increasing cure time, cure enthalpy was decreased and a negative, while cure enthalpy was a positive value in 35-NR and 35-NR/RNR when cure time was over 35 minutes due to the reversion. Swell index (Si) was gradually decreased but increased slightly in the case of both NR and NR/RNR cured for 35 minutes. The study also indicated that cure enthalpy data was very precise and fast to predict the cure state of the NR and NR/RNR blend.

Key words: Recycled Natural Rubber, Exothermic Reaction, Vulcanization, Cure Enthalpy

INTRODUCTION

The rubber industry began when Goodyear developed the first useful rubber compound: natural rubber plus sulfur [1,2]. The concept of mixing materials into rubber to improve performance is still of primary importance today. Without compounding, few rubber goods would be of any commercial value.

In the process of manufacturing a final product, the cure extent of rubber compound, with an aim to impart a certain crosslink density, plays an important role in its performance. It has long been known that most of the performance properties show a maximum at a certain degree of cure. Mechanical properties of the material are strongly dependent on the crosslink density of rubber. Modulus and hardness increase monotonically with increasing crosslink density, and the material becomes more elastic, or stated alternatively, less hysteric. Fracture properties, such as tear and tensile strength, pass through a maximum as crosslinking is increased. Elastomers have an optimum crosslink density range for practical use. Crosslink levels must be high enough to prevent failure by viscous flow, but low enough to avoid brittle failure [3].

In the same way as for thermosetting resins [4], the process of curing rubbers is rather complex, since it consists of the stages of heat transfer through the rubber and internal heat generated by the overall cure reaction. The cure reaction is highly complex and the reaction starts at a given temperature depending on the nature of the vulcanizing agent. Thus, the rubber is heated in the mould at a temperature for which the reaction takes place. The cure of rubbers is of great importance from the economic point of view, since a product badly cured with poor mechanical properties cannot be recycled and hence should be rejected.

The determination of the kinetics of cure is of great interest, as this kinetics is the basis for evaluating the operational conditions of the cure: temperature and time for a given dimension of the sample. Rheometers are widely used, especially the moving die rheometer (MDR) introduced in 1985 [5]. The rheometer is used at various temperatures, and thus the temperature-dependence of the process can be obtained [6]. Two experimental limitations, however, can be considered: (i) The one with the temperature range over which meaningful data can be obtained. The lower temperature for cure studies leads to very long times. The higher temperature is determined by the induction period for the cure reaction to initiate. Thus, it can be said that a temperature window of around 20-30 °C width is found, over which meaningful data can be obtained. (ii) Another problem appears with the temperature of the sample. In isotherm MDR, the applied temperature is the set apparatus temperature and not the true sample temperature, especially in the following cases. At the beginning, a sample at room temperature is introduced into the slabs of the MDR kept at the selected temperature and it takes some time for the equilibrium in the sample to establish. Because of local heating arising from the exothermic reactions, some gradients of temperature are developed through the sample, especially when the cure enthalpy is not very low. Nevertheless, the kinetic parameters of the overall cure reaction can be determined from the MDR experiments, such as the energy of activation and the pre-exponential factor, the order of the reaction (often taken as one), but the cure enthalpy is not obtained.

Researchers are engaged in the process of optimizing the extent of cure with an objective to enhance productivity and quality of a product. An attempt has been made to apply a differential scanning calorimetry (DSC) technique to understand the state of cure of rubber compounds. When an uncured compounded rubber is subjected to a time-temperature program in DSC, an exotherm (ΔH, enthalpy) is observed based on the nature of the polymer, curatives and other additives in the matrix. When the same compound is step cured for different times at a fixed temperature and then subjected to a similar temperature scan in DSC, H reduces and tends to zero with the extent of cure. When the matrix is fully cured, i.e., no more crosslink-

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[†] To whom correspondence should be addressed.
E-mail: eklee@cju.ac.kr

ing takes place, then instead of exothermic, sometimes we get endothermic behavior, depending on the nature of polymer and its tendency to reversion.

Various other standard ASTM test methods of measuring state of cure require evaluation of properties such as tensile, modulus, elongation, hardness, compression set and, in some cases, cold temperature brittleness.

All tests require either ASTM slabs or buttons. Moreover, all these processes are very tedious, time consuming and involve huge cost. Sometimes, many approximations are also required to get the required results.

In the present study, an attempt has been made to develop and apply a DSC technique, which is very fast and precise, to understand the state of cure and optimize the cure cycle of a rubber product. The method is based on the value of the exotherm obtained in the temperature region of approximately 100-300 °C at a scan rate of 20 °C under inert atmosphere.

EXPERIMENTAL

1. Materials and Formulations

The natural rubber used in this study was Standard Malaysian Rubber (SMR L). The recycled natural rubber powder (RNRP) was used. All other ingredients, such as sulfur, stearic acid and zinc oxide, fast extrusion furnace (FEF) and dioctyl phthalate (DOP) were of commercial grade and were used without further purification. The formulations and designation are given in Table 1. The samples are designated as a-NR and a-NR/RNR; a refers to the cure time applied.

2. Mixing and Molding

Two rubber compounds were prepared in a 1.6 liter laboratory banbury mixer with a fill factor of 0.8. Compounding was carried out in two stages. In the first stage, rubber was mixed with all other ingredients except the curing agent, sulfur. The mixing was done at 60 rpm rotor speed for 5 minutes and subsequently sheeted out on a two-roll mill. The specification of the mill was as follows: length, 0.45 m; radius, 0.10 m, speed of slow mill, 20 rev min^{-1} and gear ratio, 1.4. The compounded rubber was left for at least 24 hours for maturation and mixed with the curing agent in the final stage where final batch mixing was done at 25 rpm for 4 minutes. The rubber sheets (3 mm thick) were compression molded at 145 °C in various states of cure by varying cure time from 15 minutes to 35 minutes with an internal of 5 minutes. The compression-molded samples were immediately quenched in ice water to prevent them from further curing.

3. Cure Enthalpy Measurement and Crosslink Density

Cure enthalpy was measured by using a Perkin Elmer DSC 6. A certain mass of sample in the range of 15-20 mg was encapsulated in a sample pan and scanned from 150-300 °C at a scan rate of 20 °C/min under nitrogen atmosphere.

The procedure for the determining the crosslinking density (CD) involves the swelling of a weighted sample of rubber in toluene for approximately 48 hours. The rubber is removed, blotted quickly with filter paper and weighed in a weighing bottle. Swelling index is defined as the ratio of swollen weight to initial weight of the test sample. After removal of the solvent in a vacuum oven, the weight of imbibed solvent is obtained as the difference between the weight of swollen sample and dried sample. The extent of swelling is given by the volume fraction of the rubber (V_r) in the swollen gel and is calculated by using the method of Ellis and Welding [7].

$$V_r = \frac{(D - FA)\rho r - 1}{(D - FA)\rho r - 1 + A0\rho s - 1}$$

where, D=swollen weight, F=fraction insoluble, A=sample weight, A0=weight of the absorbed solvent corrected for swelling increment, ρr=density of rubber and ρs=density of solvent.

The crosslink density is calculated from V_r by means of the Flory-Rehner relationship [8].

$$CD = \frac{[-\ln(1 - V_r) + V_r + \chi V_r^2]}{(2\rho V)V_r^3}$$

where, χ=polymer-solvent interaction parameter, ρ=density of polymer and V=molar volume of solvent.

4. Mechanical Properties

Dumb-bell-shaped samples were cut from the molded sheets according to ASTM D 412. Tensile testing of the samples were carried out using an Instron Universal Testing Machine (4444-C10283) at a cross-head speed of 50 mm/min and at 25±2 °C. The hardness of the samples was measured as per ASTM D-2240 with a Mitutoyo Shore A meter. For hardness measurements, sheets having an effective thickness of 6 mm were used.

RESULTS AND DISCUSSION

Sulfur vulcanization can be divided into two steps: (a) induction period when the rubber, sulfur, accelerator, and activator are reacting to produce the intermediates that will eventually give rise to crosslinks, and (b) first order exothermic crosslinking reaction, which leads to an increase of torque or modulus. Because of this exothermicity of

Table 1. Formulations and designation of the NR and NR/RNR blends

Ingredients	NR (phr)[a]	NR/RNR (phr)[a]	Sample code	
Natural rubber (SMR L)	100	50	15-NR	15-NR/RNR
Recycled natural rubber (RNR)	-	50	20-NR	20-NR/RNR
Stearic acid	3	2	25-NR	25-NR/RNR
Zinc oxide	5	4	30-NR	30-NR/RNR
Semi reinforcing furnace (SRF)	60	40	35-NR	35-NR/RNR
Process oil	40	20	*a*-NR and *a*-NR/RNR; *a* refers	
Sulfur	0.6	0.4	to cure time	

[a] Parts per hundred rubber

the vulcanization reaction, true isothermal conditions are never established in a vulcanizing elastomer system. Moreover, vulcanization processes are extremely complex, involving numerous consecutive and simultaneous reactions.

1. Differential Scanning Calorimetry

DSC is a thermal technique capable of detecting endothermic and exothermic characteristics of elastomeric systems. The observed enthalpy as obtained by DSC is the mathematical sum of the enthalpies of all individual reactions occurring in the temperature range of measurement.

In a first order reaction like sulfur vulcanization of natural and synthetic rubber, the following conversion is assumed for a peak observed on the DSC curve when the sample is subjected to a controlled temperature heating:

$$A \xrightarrow{k} B + \Delta H$$

where, k=velocity constant or specific reaction rate constant and ΔH=heat of reaction or cure enthalpy.

Fractional conversion (X_n) is defined as:

$$X_n = \frac{\Delta H_u - \Delta H_{ct}}{\Delta H_u}$$

where, ΔH_u=enthalpy of uncured compound, ΔH_{ct}=enthalpy of compound cured for time, t.

Residual heat of vulcanization ($1-X_n$) is proportional to the unreacted cure system and is a function of time.

DSC characteristics obtained for all step cured samples from NR and NR/RNR blend are shown in Table 2. It is observed in both NR and NR/RNR that the absolute value of the enthalpy decreases as the state of cure expressed in cure time increases. This is because of the presence of much less rubber matrix, which can participate in the vulcanization as the state of cure increases. Meanwhile, cure enthalpy generated from NR is bigger than that from NR/RNR blend for the same cure time due to the more rubber matrix to show exothermic reaction in the vulcanization. Only one positive value, found in the case of NR and NR/RNR blend cured for 35 minutes, may be due to the reversion (endothermic) process, a common phenomenon observed with natural rubber when it is over-cured [9].

Cure enthalpy is greatly affected with amount and/or type of ingredients. Therefore, the composition of each sample should be considered for comparison. This is evident when individual cure enthalpies from the two samples, NR and NR/RNR, are looked into separately. A considerably high value of cure enthalpy is observed with the 100% NR formulation (NR) as compared to that observed with NR/RNR blend. This ΔH trend, which is considered to be enough to support the trend of V_r value, crosslink density and other mechanical properties with cure state expressed in time, helps us to predict the extent of cure accurately.

Table 2. DSC characteristics of the NR and NR/RNR blends

Sample	Cure enthalpy (ΔH, J/g)	Fractional cure ($Xn=(\Delta H_u-\Delta H_{ct})/\Delta H_u$)	Residual cure ($1-X_n$)
0-NR	−12.45	-	-
15-NR	−3.327	0.774	0.226
20-NR	−2.287	0.824	0.176
25-NR	−0.913	0.929	0.071
30-NR	−0.016	0.968	0.032
35-NR	+0.024	1.008	−0.008
0-NR/RNR	−7.32	-	-
15-NR/RNR	−2.673	0.786	0.214
20-NR/RNR	−1.354	0.863	0.137
25-NR/RNR	−0.658	0.934	0.066
30-NR/RNR	−0.056	0.976	0.024
35-NR/RNR	+0.026	1.010	−0.010

2. Swelling Behavior

For the purpose of supporting and correlating DSC cure enthalpy findings, crosslink density by equilibrium swelling measurements was also performed to judge the state of the degree of vulcanization. Fig. 1 shows the values of swell index, S_i, of all step-cured samples, NR and NR/RNR blend. The swelling index value decreases with the increasing degree of cure. As the crosslinking of rubber is increased more and more, three-dimensional network structures are formed that restrict swelling in the solvent. In this way, when the

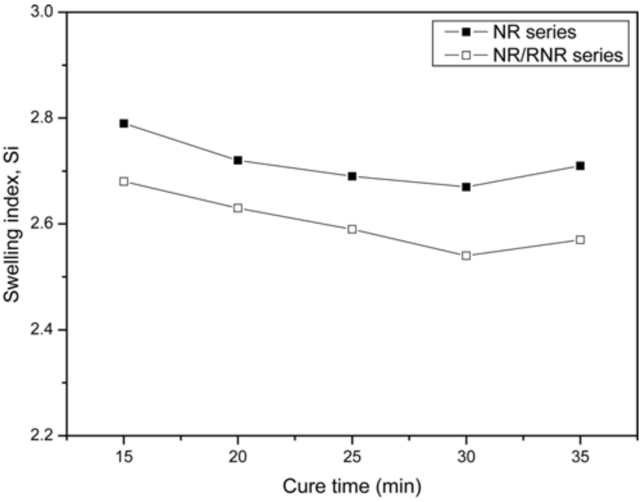

Fig. 1. Variation of swelling index of the NR and NR/RNR as a function of cure time.

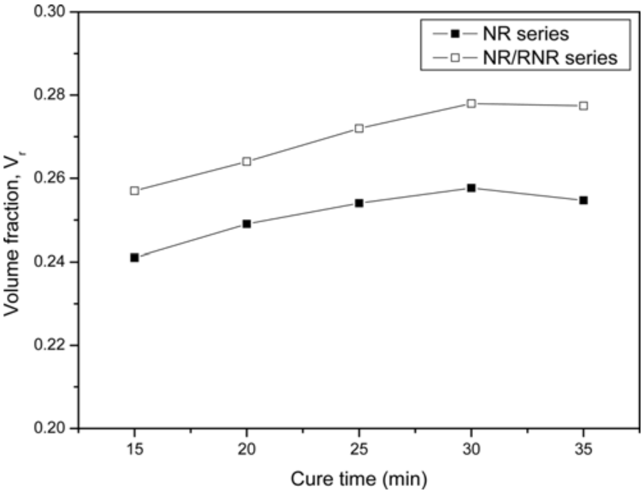

Fig. 2. Variation of volume fraction of the NR and NR/RNR as a function of cure time.

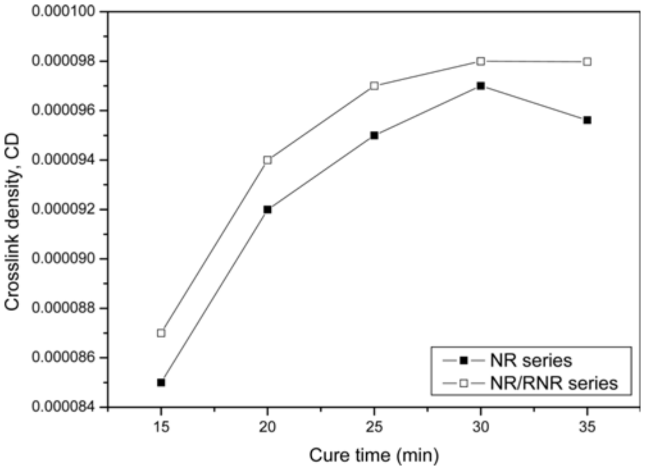

Fig. 3. Variation of crosslink density of the NR and NR/RNR as a function of cure time.

Table 3. Mechanical properties of the NR and NR/RNR blends

Sample	100% Modulus (MPa)	200% Modulus (MPa)	300% Modulus (MPa)	Tensile strength (MPa)	Hardness (duro A)
15-NR	2.5	6.6	12.0	24.7	61
20-NR	2.8	7.4	13.1	25.0	62
25-NR	2.8	7.5	13.3	25.4	63
30-NR	2.7	7.2	12.9	25.9	64
35-NR	2.7	7.2	12.8	25.6	64
15-NR/RNR	2.1	6.2	11.4	22.3	64
20-NR/RNR	2.3	6.6	11.7	22.7	65
25-NR/RNR	2.4	6.8	11.9	23.2	66
30-NR/RNR	2.6	7.1	12.2	23.7	68
35-NR/RNR	2.5	6.9	12.1	23.6	68

crosslinking is increased further, the gel point is eventually reached, and the whole composition no longer dissolves in the solvent. Compared with NR, the NR/RNR blend gives greater swelling resistance. This is due to the presence of crosslinked precursors and unreacted curative in rubber matrix of NR/RNR blend, which might reduce the penetration of solvent into the NR/RNR compound. Volume fraction (Fig. 2) and crosslink density (Fig. 3), which can be expressed as the reciprocal of swelling index value, pass through a maximum as crosslinking is increased.

3. Mechanical Properties

Mechanical properties, such as tensile strength, modulus and hardness with increasing cure time, are presented in Table 3. The general tend is: with increasing cure time, increased hardness as a function of increased vulcanization is observed in all cases.

The tensile strength gradually increased to a maximum at 30-minute cure time in both NR and NR/RNR blend. Further increase of cure time leads to a decrease in tensile strength. This reversion phenomenon occurring in natural rubbers which are sulfur vulcanized and overcured is prominent, i.e., destruction of crosslinks predominates over the usual bond formation while curing. The main parameter governing reversion stability is the number of double bonds along the longitudinal axis of the macromolecule. During vulcanization, the crosslinks initially formed are mainly the thermally unstable polysulphidic bonds. These are transformed into di- and monosulphidic crosslinks as the cure progresses. Reversion is the loss of some of the original polysulphides due to the secondary reactions of the S_8 crosslinks which are initially formed. The liberated sulfur, or the sulfur which is still present in the vulcanizates, may result either in post vulcanization or modification to the polymer chain leading to lower mechanical properties of natural rubber product. Compared with NR, the NR/RNR blend gives lower tensile strength due to the weak interaction and bonding between the recycled rubber powder particles and the natural rubber matrix when more than 10 phr is used [10].

Modulus of the samples, NR and NR/RNR increases with cure time up to 30-NR and 30-NR/RNR and it is found to be decreased in 35-NR and 35-NR/RNR. With increasing cure time, more and more crosslinks are formed, attain a maximum and then start decreasing when cure time is over 30 minutes. This trend is very similar to that of tensile strength of NR and NR/RNR. Therefore, maximum physical properties are attained at 30 minutes cure time. DSC study also points towards similar findings. This corresponds to about 90% achievement of state of cure. By comparing these two findings, technically one can predict how much time is to be provided in the process of curing in order to get a quality product.

CONCLUSION

The absolute value of the enthalpy decreases as the state of cure expressed in cure time increases in both NR and NR/RNR. Meanwhile, cure enthalpy generated from NR is bigger than that from NR/RNR blend for the same cure time. Only one positive value, found in the case of NR and NR/RNR blend cured for 30 minutes, may be due to the reversion (endothermic) process. The swell index decreases with the increasing cure time. Compared with NR, the NR/RNR blend gives greater swelling resistance due to the presence of crosslinked precursors and unreacted curative in rubber matrix of NR/RNR blend. Volume fraction and crosslink density, which can be expressed as the reciprocal of swelling index value, pass through a maximum as crosslinking is increased. With increasing cure time, increased hardness as a function of increased vulcanization is observed in all cases. The tensile strength gradually increased to a maximum at 30-minute cure time in both NR and NR/RNR blend. Further increase of cure time leads to a decrease in tensile strength. Compared with NR, the NR/RNR blend gives lower tensile strength due to the weak interaction and bonding between the recycled rubber powder particles and the natural rubber matrix when more than 10 phr is used. Modulus of the samples, NR and NR/RNR increases with cure time up to 30-NR and 30-NR/RNR and it is found to be decreased in 35-NR and 35-NR/RNR.

REFERENCES

1. C. Goodyear, U.S. Patent 3,663 (1844).
2. C. Goodyear, *Gum elastic*, New Heaven (1855).
3. M. Akiba and A. S. Hashim, *Prog. Polym. Sci*., **22**, 475 (1997).
4. D. H. Kim, J. O. Beak, Y. S. Choe and W. H. Kim, *Korean J. Chem. Eng*., **22**, 755 (2005).

5. I. D. Rosca and J. M. Vergnaud, *Polymer*, **43**, 195 (2002).
6. E. K. Lee and S. Y. Choi, *Korean J. Chem. Eng.*, **24**, 1070 (2007).
7. B. Ellis and G. N. Welding, *Rubber Chem. Technol*., **37**, 563 (1964).
8. D. De and A. N. Gent, *Rubber Chem. Technol*., **69**, 834 (1996).
9. Indian Rubber Institue, *Rubber engineering*, 1st edn., pp. 299-300, M. M. Patel et al., eds., McGraw-Hill, New York (1998).
10. H. Ismail, R. Nordin and A. M. Noor, *Polymer Testing*, **21**, 565 (2002).