

A Kinetic and Rheometric Investigation of Hexamethylol Melamine Derivative on the Cure of Natural Rubber Compounds

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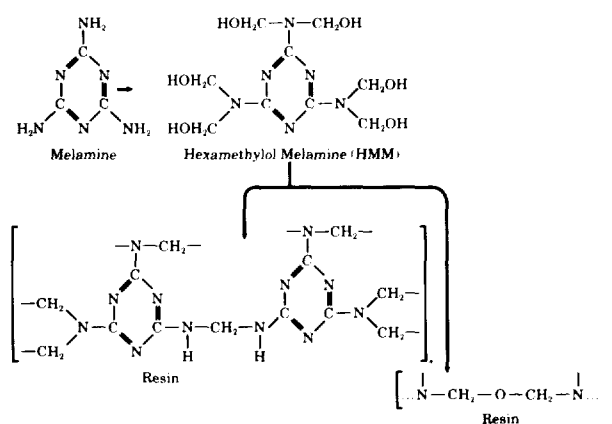
SYNOPSIS

Hexamethylol melamine (HMM) was characterized by Fourier transform infrared (FTIR) spectroscopy. The optimum dose of HMM in the presence of a sulfur accelerator in a natural rubber (NR)-filled compound was determined. The cure rate and kinetics of crosslink formation indicate that HMM enhances the first-order rate of vulcanization in an NR compound. The results reveal good mechanical properties of an HMM-based NR carbon black-filled vulcanizate. © 1997 John Wiley & Sons, Inc.

INTRODUCTION

Resins are used as compounding ingredients for elastomers to improve the properties of the vulcanizate. Some resins are used as curing agents for the resin-cure vulcanization of elastomers. Tawney *et al.*¹ showed that with the methylol resin system the rate of vulcanization is considerably slower than in the sulfur system but it imparts a greater stability toward prolonged vulcanization. It also showed marked improvement in the rate and state of cure through the catalyzing action of metallic halides. Subsequently, a number of works have been reported for the catalytic activation of the methylol resin cure with polychloroprene rubber, chlorosulfonated polyethylene, chlorinated waxes, and halogenated butyl rubbers² and on the mechanism of the reactions.³⁻⁷ Recently, Sato⁸ prepared HMM by reacting melamine with formaldehyde and studied the reaction kinetics. The present communication reports a critical study on the role of hexamethylol melamine (HMM) in rubber vulcanization.

Melaminelike urea reacts with formaldehyde under neutral or slightly alkaline condition to yield HMM.^{9,10} The material has no definite melting point and is very stable and is resinified through methylene and ether linkages⁹:



There is only report¹¹ on HMM which deals only with the good cure, mechanical properties, and wire adhesion of rubber. The present work is a critical study of HMM on the kinetic and rheometric properties for crosslink formation and the physical properties of the vulcanizate in a natural rubber (NR) compound formulation.

EXPERIMENTAL

Hexamethylol Melamine (HMM) Synthesis¹²⁻¹⁴

A three-necked round-bottom flask was fitted with a stirrer and reflux condenser. To formaldehyde (360 g, 37% w/w formaline), which was neutralized with a sodium carbonate solution, was added melamine (63 g). The mixture was heated at 70°C for 2 h. It

Table I Mix Formulation for NR Compound

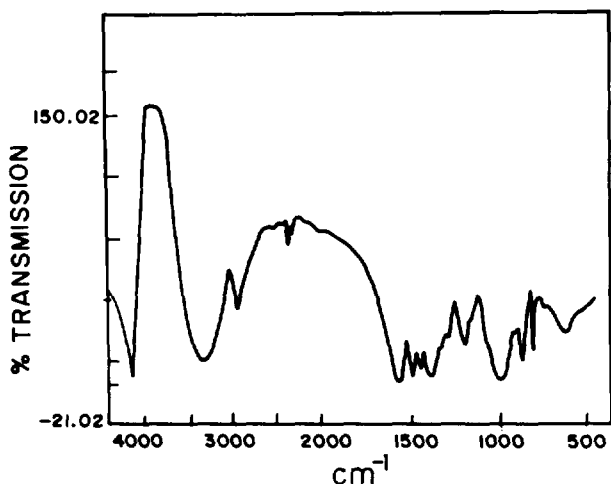
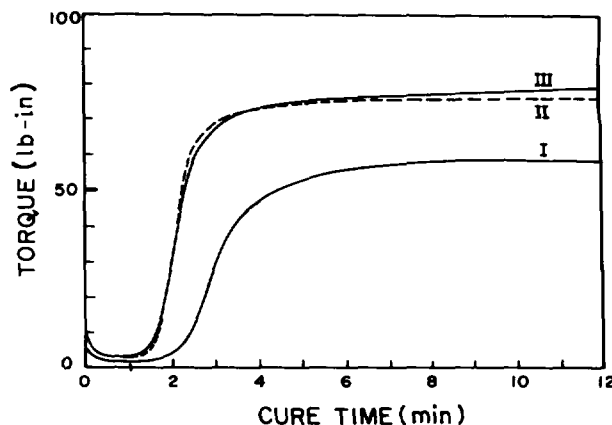
| Ingredients | S-I | S-II | S-III |
|----------------------|--------|--------|--------|
| RMAI | 100.00 | 100.00 | 100.00 |
| Zinc oxide | 5.00 | 5.00 | 5.00 |
| Stearic acid | 2.00 | 2.00 | 2.00 |
| Carbon black (N 330) | 55.00 | 55.00 | 55.00 |
| HGN | 0.50 | 0.50 | 0.50 |
| BSM | 0.90 | 0.90 | 0.90 |
| MBTS | 1.75 | 1.75 | 1.75 |
| Hexamine | — | 1.60 | 1.60 |
| HMM | — | 2.50 | 5.00 |

was then cooled, the resulting viscous mass was dissolved in methanol, and the solution acidified with an oxalic acid solution (5%). It was heated again at 70°C for 1 h, then cooled and made alkaline (pH 9) with 10% aqueous NaOH. The alkaline solution was distilled under reduced pressure at 50°C to yield HMM. The resulting solid was washed with water and dried.

Compounding and Testing

The NR (HMM 1; obtained from the Kerala Rubber Board, India) used had a Mooney viscosity ML 1 + 4 (100°C) of 72. The other compounding ingredients were as follows: zinc oxide (98% purity); stearic acid (Rubo Chem Industries); BSM (Accicure BSM), MBTS (Accicure MBTS), and Antioxidant (Accinox HFN) (all, I.C.I. Ltd., India); sulfur (98%; Standard Chemicals); and carbon Black (N 330; Phillips Carbon Black Ltd., India).

The NR-loaded formulations (Table I) were evaluated to determine the optimum concentration of the HMM in the vulcanization reaction under stan-

**Figure 1** FTIR spectra of HMM.**Figure 2** Rheometric curve of HMM-filled NR compounds.

dard conditions. The recipes differed only in the dose of HMM. After determining the optimum concentration, three samples were chosen for investigation: S-I without HMM, S-II with the optimum dose, and S-III for a higher dose of HMM.

The optimum cure time and other cure characteristics for various mixes at 150°C were evaluated using a Monsanto rheometer (R-100) according to ASTM Standard D 2084-88. The cure rate index and cure kinetics were determined from the rheographs of the respective compounds.

All compounds were prepared on a laboratory-size two-roll mixing mill (30 × 15 cm) at a friction ratio of 1 : 1.25, according to the procedure given in ASTM D3185-88. The test specimen vulcanization was carried out in 18 in. (460 mm) × 18 in. (460 mm) platens using an electrically heated press maintained at 150°C, 45 kg/cm² pressure.

Tensile properties were determined according to ASTM Standard D 412-87 with dumbbell specimens in an Instron Universal Tensile tester machine 4301

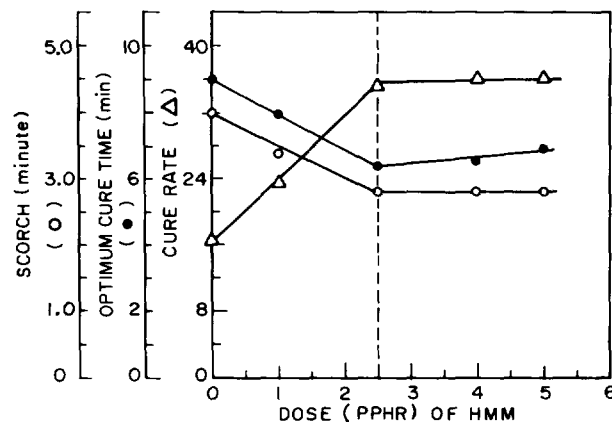
**Figure 3** Optimum dose of HMM in presence of BSM-MBTS in standard NR compound.

Table II Curing Kinetics of HMM for NR Compounds as Studied by Monsanto Rheometer at 150°C

| S-I | | S-II | | S-III | |
|------|---------------------------|------|---------------------------|-------|---------------------------|
| t | $\log (R_{\infty} - R_t)$ | t | $\log (R_{\infty} - R_t)$ | t | $\log (R_{\infty} - R_t)$ |
| 4.0 | 1.75 | 2.8 | 1.87 | 2.8 | 1.88 |
| 4.8 | 1.70 | 3.6 | 1.79 | 3.6 | 1.80 |
| 5.6 | 1.57 | 4.4 | 1.54 | 4.4 | 1.51 |
| 6.4 | 1.41 | 5.2 | 1.28 | 5.2 | 1.26 |
| 7.2 | 1.27 | 6.0 | 1.08 | 6.0 | 1.13 |
| 8.0 | 1.14 | 6.8 | 0.95 | 6.8 | 1.06 |
| 8.8 | 1.00 | 7.6 | 0.81 | 7.6 | 1.00 |
| 10.4 | 0.85 | 8.4 | 0.74 | 8.0 | 0.97 |

at a pulling rate of 500 mm per min at room temperature (30°C). Hardness was measured according to ASTM D 2240-86.

RESULTS AND DISCUSSION

FTIR Spectra

The spectra of the melamine derivative is shown in Figure 1. The absorption band in the range of 3500–3700 cm^{-1} is due to the presence of hydroxyl groups. As expected, the absorption band in the range 3500–3700 cm^{-1} is assigned to the characteristic hydroxyl groups formed due to the reaction.

Kinetic and Rheometric Investigations

Investigation of the reactivity order of HMM indicates that the material containing hydroxyl groups is reactive in the NR vulcanizate in the presence of

the sulfur–accelerator system. The rheographs (Fig. 2) clearly indicates that HMM improves the reactivity order sharply compared to the sulfur–accelerator system.

Optimum Dose

The optimum dose of HMM in the presence of the sulfur–accelerator was shown to be 2.5 phr in the NR-filled compound (Fig. 3), beyond which the curve criteria show a sharp change.

Relative Cure Rate and Scorch

From Figure 2, it may be inferred that HMM has an accelerating effect on NR vulcanization with the sulfur–accelerator system. This behavior could possibly be explained by the formation of an intermediate *in situ* in the rubber matrix with hydroxyl groups of HMM, thus enhancing the rate of reaction.

Table III Curing Characteristics and Physical and Mechanical Properties of HMM-filled NR Compounds*

| Properties | S-I | S-II | S-III |
|--|--------|--------|--------|
| Rheometric | | | |
| Max torque (lb-in.) | 61 | 76 | 77 |
| Optimum cure time (min) | 9 | 6.4 | 7.0 |
| Scorch time (min) | 4 | 2.8 | 2.8 |
| Cure rate index (min^{-1}) | 20 | 27.5 | 24.0 |
| First-order specific rate constant (K) | 0.1794 | 0.2391 | 0.3235 |
| Physical | | | |
| Tensile strength (MPa) | 16.16 | 13.86 | 11.75 |
| First modulus (MPa) | 1.69 | 1.75 | 1.64 |
| Elongation at break (%) | 964 | 807 | 741 |
| Energy at test end (J) | 12.48 | 10.25 | 7.87 |
| Hardness (Shore A; °) | 67 | 70 | 72 |

* Cure condition: temperature 150°C; pressure 45 kg/cm^2 .

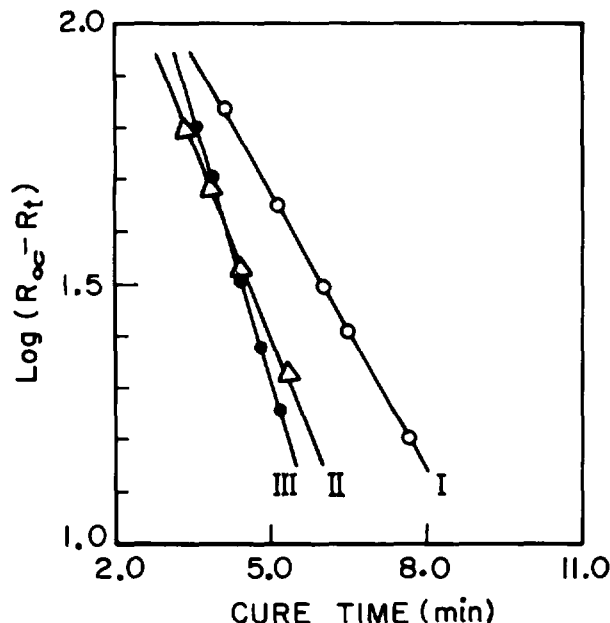


Figure 4 $\text{Log}(R_\infty - R_t)$ vs. cure time for HMM-filled NR compound.

Cure Properties and Crosslink Formation

We adopted Coran's model¹⁵ to evaluate the crosslink formation. According to this model, the crosslink formation kinetics is first order after an induction period, t_i :

$$\frac{dV_u}{dt} = K(V_{u_\infty} - V_u) \quad (1)$$

V_{u_t} and V_{u_∞} are the crosslink density at time t and after completion of the cure and t_i is the delay time. On integration, eq. (1) gives

$$V_{u_t} = V_{u_\infty} \{1 - e^{-K(t-t_i)}\},$$

or

$$\ln(V_{u_\infty} - V_{u_t}) = \ln V_{u_\infty} - K(t - t_i) \quad (2)$$

The rheometer torque is proportional to crosslink density (V_{u_t}). The constant of proportionality changes with different stocks. So, at any rate, the increase in the torque reading can be considered as a measure of the relative crosslink density.

Therefore, eq. (2) gives

$$\ln(R_\infty - R_t) = -K(t - t_i) + \ln R_\infty \quad (3)$$

The plot $\ln(R_\infty - R_t)$ vs. t gives a straight line, the negative slope of which gives the first-order specific rate (K) of the crosslinking reaction.

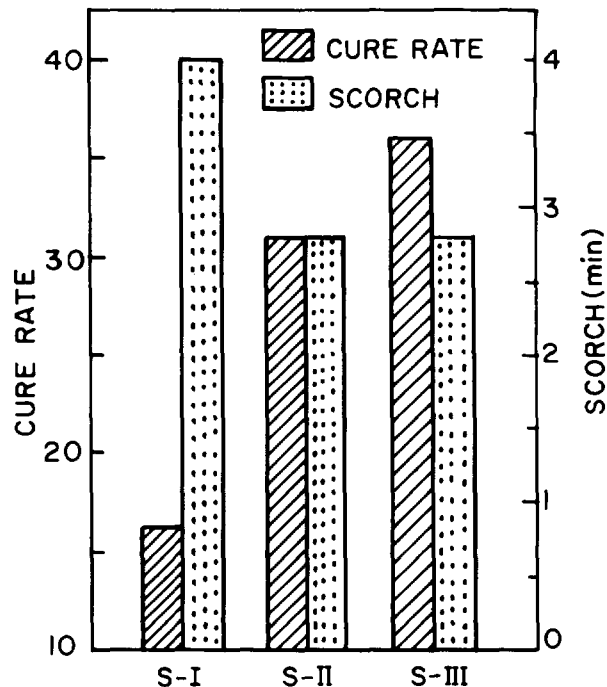


Figure 5 Relative cure rate and scorch at 150°C of HMM-filled NR compound: (a) time for 2×10^{-1} Nm rise of torque over minimum; (b) slope of the ascending portion of the rheogram.

The observed test results depicted in Tables II and III and Figures 4 and 5 show that the crosslink density increases with the use of HMM in the sulfur-accelerator NR black-filled vulcanizate. The compounds using HMM show a fast cure rate and give a vulcanizate of high crosslink densities.

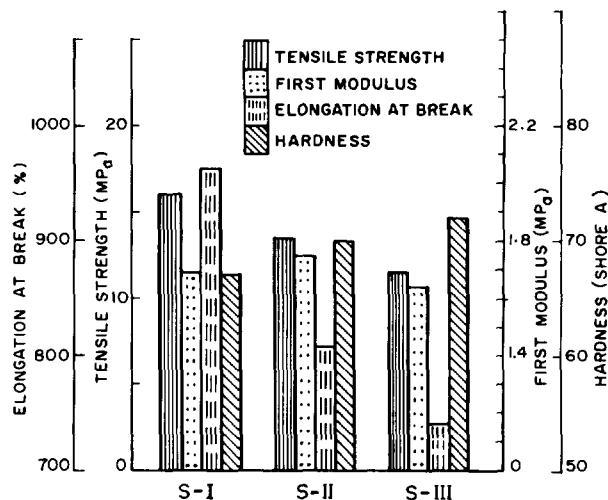


Figure 6 Physical and mechanical properties of HMM-filled NR vulcanizate.

Physical and Mechanical Properties of Vulcanized NR System

The physical and mechanical properties of vulcanized NR samples containing HMM are summarized in Table III and Figure 6. The tensile strength and elongation at break decrease with increasing dose of HMM. The higher strain (100%) moduli increase with the addition of HMM (2.5 phr optimum), but decrease at higher doses. The HMM vulcanized samples show an increase in hardness. It is well known that compounding which produces an increase in hardness also produces increases in higher strain moduli values. The HMM vulcanized samples show that one part of HMM is required to increase hardness by 1° for black-filled NR over the central part of the hardness range of 50°–80° Shore A.

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