

Woven Fabric-Elastomer Laminate. I. Thermal Analysis of Cure Characterization of Fluorocarbon Elastomer Coatings

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ABSTRACT: Cure characterization of fluorocarbon elastomer coatings has been analyzed by differential scanning calorimetry. The composition of these coatings include Viton GF, peroxide, triallylisocyanurate, sublimed litharge (PbO), carbon black, and solvent. Five different formulations of these compounds have been reported and explored. Kinetic studies indicate that the cure was completed in 3 min at an isothermal curing temperature of 180°C. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 551–554, 1997

Key words: woven fabric laminate; fluorocarbon elastomer; elastomer coating; cure characterization; rubber composite

INTRODUCTION

Since the middle 1950s, fluorocarbon elastomers have been widely used for severe heat and chemical resistance applications. Most commercially available fluorocarbon elastomers consist of copolymers of vinylidene fluoride (VF₂) with hexafluoropropylene (HFP) and, optionally, tetrafluoroethylene (TFE).^{1,2} There are also many other combinations such as perfluoromethyl vinyl ether (PMVE), chlorotrifluoroethylene, and others. These fluorocarbon elastomers have relatively higher contents of fluorine (about 53–70 wt %), which provide remarkable resistance to flame, chemicals, solvents, and oxidative attack.³

In this article, we intend to establish a relationship between cure behavior and end use properties of fluorocarbon elastomer coatings. Cure in-

formation for rubber stock, measured by an oscillating disk rheometer (ODR), is inadequate to describe the chemical kinetics for coatings. As Uschold has noted,⁴ fluorocarbon elastomers may be cured with nucleophilic curatives such as diamines or bisphenols. The mechanism of cross-linking reveals that, although the cured parts possess excellent physical properties, double bonds still remain on the backbone that may serve as potential sites for degradative side reactions with steam, hot water, acids, or other chemicals. To overcome this drawback, the peroxide curing system was suggested.² Some special monomers such as CF₂=CFBr, CF₂=CFI, or CH=CHCF₂CF₂Br were added to the fluorocarbon elastomer backbone. These monomers served as cure sites when the fluorocarbon elastomer was cured with peroxides.^{5,6} Since fluorocarbon elastomers cured with peroxides generally provide higher strength and exceptionally good resistance to oils and organic fluids, hot water, steam, inorganic acids, and other aqueous media,⁷ a comprehensive understanding of their cure characterization is worth exploring.

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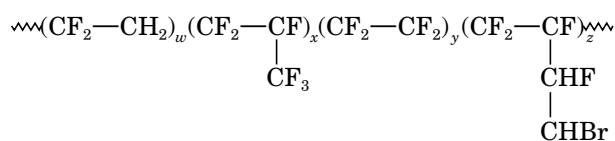
Table I Polymers and Compounding Ingredients

Ingredient Used	Description	Suppliers
Viton GF	—VF ₂ —HFP—TFE—CSM—	E. I. Du Pont
Thermax MT	MT Carbon Black (N990)	Cancarb Ltd.
Sublimed Litharge	PbO	R. D. H.
TAIC	Triallylisocyanurate	Nippon Kasei Chem.
Perhexa 2.5B	2,5-Dimethyl-2,5-bis(<i>t</i> -butyl peroxy) hexane	Nippon Oil & Fast Co. Ltd.
MEK	Methyl Ethyl Ketone	Union Chem. Works Ltd.

EXPERIMENTAL

Materials

Viton GF is a popular member of the family of peroxide-curable fluorocarbon elastomers, and its typical structure is given below.



w, *x*, *y*, and *z* are integers

Other compounding ingredients and their suppliers are summarized in Table I, where 2,5-dimethyl-2,5-bis(*t*-butylperoxy)hexane (Perhexa 2.5B) is a curing agent, Thermax MT (carbon black) a filler, and triallylisocyanurate (TAIC) and sublimed litharge (PbO) are coagent and acid acceptor, respectively. These are major components generally adopted in practical application.²

Compounding

The compositions of five formulations are listed in Table II.

Coating Paste Preparation

Since the commercial fluorocarbon elastomers are easily processible using standard equipment such as two-roll mills and internal mixers, a banbury has been chosen for the mastication of rubber gum stock.

Viton GF was first masticated in a banbury for 20 min at room temperature. The compound was then sheeted out and cut into small pieces to increase the solution rate in methyl ethyl ketone. When the Viton GF had completely dissolved, other ingredients including carbon black, curing agent, and metallic oxides were added to the Viton GF solutions and thoroughly mixed.

Thermal Measurements

The coating sample was first heated under vacuum for 15 min at 45°C (elimination of MEK) and 85°C (elimination of water) before it was sealed in an aluminum pan with a perforated lid. The sample pan was placed in a differential scanning calorimeter (DSC) cell (Du Pont 930 differential calorimeter) under a 50-cm³/min dry nitrogen purge. Isothermal scanning was performed at 150, 160, 170, and 180°C. Establishment of a temperature equilibrium at the beginning of each cure experiment is necessary. Thus the residue exotherm must be calibrated for each dynamic

Table II Compositions of Five Formulations

Compound (unit : phr)	A	B	C	D	E
Viton GF	100	100	100	100	100
Triallylisocyanurate	3	3	3	4	5
Organic Peroxide	2	2	2	2	2
Sublimed Litharge	3	3	3	3	3
MT Carbon Black (N990)	20	30	40	30	30
MEK	450	450	450	450	450

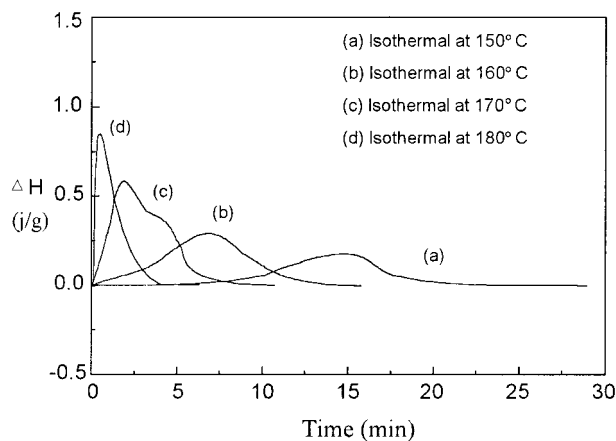


Figure 1 A family of thermograms at isothermal temperatures of 150, 160, 170, and 180°C for formulation C.

scanning to improve the accuracy of the isothermal method (in other words the baseline must be rerun for each scanning).

RESULTS AND DISCUSSION

Figures 1 and 2 are plots of ΔH versus time and ΔH versus temperature, respectively, for the exothermic cure reaction of a typical formulation C. For analysis of these kinetic data, we have adopted a general equation [eq. (1)] to illustrate the cure process.⁸

$$d\alpha/dt = r = kf(\alpha) \quad (1)$$

where r is reaction rate, k is the rate constant, and $f(\alpha)$ represents the function of the conversion (α) at a given time and temperature.

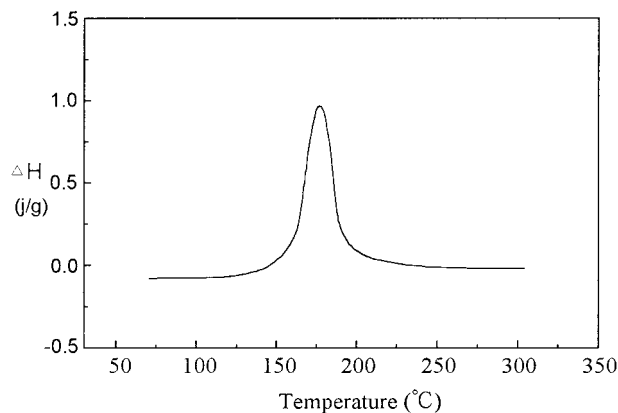


Figure 2 The exothermic reaction of formulation C.

The rate constant, k , can also be expressed as the Arrhenius form

$$k = A \exp(-\Delta E/RT) \quad (2)$$

where A is the Arrhenius frequency factor, ΔE is the activation energy, T is the absolute temperature, and R is the gas constant.

Taking the logarithm of eqs. (1) and (2), we obtain

$$\ln r_\alpha = \ln[Af(\alpha)] - \frac{\Delta E}{RT\alpha} \quad (3)$$

For any given α value (from 10 to 90%), the activation energy ΔE can be calculated as the slope [$\times(-R)$] from the $\ln r_\alpha$ versus $1/T_\alpha$ linear relationship. The isothermal measurements were taken at 150, 160, 170, and 180°C, and these results of ΔE are listed in Table III. For example,

Table III Activation Energy of Formulation A Through E at Different Conversion

Conversion (α %)	ΔE (KJ/mol)				
	A	B	C	D	E
10	156.1	148.8	133.6	158.6	154.2
20	156.1	146.2	131.9	154.3	145.5
30	139.0	143.5	123.3	142.4	145.8
40	128.7	139.9	123.2	138.0	143.2
50	123.5	135.5	122.1	134.2	140.3
60	121.3	126.1	117.5	123.6	132.6
70	113.2	123.7	113.8	117.4	122.6
80	98.1	109.3	110.9	101.3	104.1
90	87.8	101.2	105.6	85.7	80.2

when α varies from 10 to 20%, ΔE is 133.6 kJ/mol (31.9 kcal/mol) and 131.9 kJ/mol (31.5 kcal/mol), respectively. When α varies from 30 to 50%, ΔE is 123 kJ/mol (29.4 kcal/mol); 117.5 kJ/mol (28 kcal/mol) at 60% conversion; 113.8 kJ/mol (27.2 kcal/mol) at 70%; 110.9 kJ/mol (26.5 kcal/mol) at 80%; and 105.6 kJ/mol (25.2 kcal/mol) at 90% conversion for formulation C.

On the basis of our observation, which led to the ΔH versus time plot shown in Figure 1, the cure time needed at 180°C is only 3 min, which is a relatively fast one. The physical and mechanical performance of these cured products has been evaluated.⁹ Generally, they are able to meet the U.S. military specification. For example, under the testing conditions (23°C, 1 atm, 60% relative humidity), the permeability of JP-5 fuel to the five-ply laminate, which was made from formulation C coated onto nylon (66) woven fabric with 0.5 mm thickness, is 0.0020 oz/ft² 24 h (0.61 g/m² 24 h). This performance is better than the requirement of MIL-T-6396E (the permeability shall be less than 0.025 oz/ft² 24 h for fuel tank materials).

CONCLUSIONS

The cure of fluorocarbon elastomer coatings has been characterized by DSC. Kinetic studies for

five different formulations (including Viton GF, peroxide, triallylisocyanurate, sublimed litharge, carbon black, and solvent) have been explored. The results indicate that the cure process can be completed in 3 min with the isothermal curing temperature at 180°C.

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