Characterization of Fluoroelastomer Networks: II. SEC, FTIR, and ODR Analysis

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SYNOPSIS

The role of an accelerator in the nucleophilic cure of fluorocarbon compounds was further examined by preparing materials without a crosslinker. Under the previously used curing conditions, ODR reveals the formation of a secondary, accelerator-induced network that is unstable at slightly higher temperature, i.e., $\geq 190°C$. Increased crosslink density and color are observed with the cure time, indicating slow curing reactions and likely formation of conjugated unsaturation. SEC of selective solvent-soluble fractions derived from specimens obtained from the key cure stages shows initially a falling refractive-index response. However, this change is followed by a shift in MWDs toward lower average molecular weights. On the other hand, infrared examination shows a continuous increase in the 1718 cm^{-1} absorption, but no major presence for the 1680 cm^{-1} absorption seen in the previous study in the presence of a crosslinker. The concurrent increase in the 3114 cm^{-1} peak confirms the presence of a $—CF=CH—$ double bond. The solvent-soluble portions and bulk specimens have very similar infrared features. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The recent rise in underhood operating temperatures because of packaging efficiencies and the changes required by new emission standards has resulted in extreme performance demands for automotive components. The temperature changes prompted the use of elastomeric parts with better heat resistance. The utilization of improved heat-resistant fluids allows longer customer warranties. However, the new fluids also proved to be more aggressive, which led to the need for elastomers with improved chemical resistance. Also, flexible fuel requirements mandated improvements in the chemical resistance of parts that came in contact with the fuel. One class of materials that appears to offer the potential to meet all these stringent operating conditions are fluorocarbon elastomers based on vinylidene fluoride (VF$_2$).

These materials are primarily vinylidene fluoride copolymers with hexafluoropropylene (HFP) and terpolymers with HFP and tetrafluoroethylene

(TFE), all of which can have varying fluorine content and monomer composition. Additionally, the terpolymers can be modified with the introduction of cure-site monomers on the polymer backbone to provide improved low-temperature performance.[1] Currently, these basic copolymers and terpolymers are used in quantity for the manufacture of some automotive parts.

To develop the proper range of properties for use in aggressive environments, the fluorocarbon elastomers must be crosslinked. Up to now, this was done primarily with such chemical moieties as diamines,[2] dihydroxy nucleophilic compounds,[3-7] and peroxides.[8] The phenolic type of crosslinkers were studied in compounds involving phase-transfer catalysis during curing. Recent efforts were directed at improving the low-temperature performance of the dihydroxy-based materials. This activity could lead to elastomeric compounds with an excellent balance of properties.

A dihydroxy nucleophile, bisphenol AF (BPAF), has been the crosslinker of choice for fluoroelastomers, likely because of the resulting good thermal stability. Recently, Theodore and Carter[7] prepared network moieties based on fluorocarbon elastomers and the BPAF crosslinker using conditions similar

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to industrial vulcanization. This was needed because previous attempts to determine the network structure consisted primarily of model compound reactions, of model prevulcanization events, and of materials cured under conditions only approaching industrial vulcanization parameters. The intent of this prior study was to produce structures for study that were very similar to those that come in contact with aggressive fluids and fuels, such as methanol–gasoline blends.

The evolution of solid-state chemistry and the final network structure were evaluated from infrared spectra obtained of 25 μm-thick sections. These sections were produced from specimens quenched at key stages of the curing process. It was established for the first time that BPAF does, in fact, serve as a crosslinker during cure. Additionally, two types of persistent unsaturation were formed on the polymer backbone after crosslinking. On the other hand, curing for extended periods of time produced no measurable effect on the network.

Although the above findings help define the final network structure and in some respects complement the earlier contributions, there remained uncertainties about the pathway leading to the final structure. Uncertainties were also present in the assignment of infrared absorption bands at 1680 and 1718 cm^{-1} to certain unsaturated structures. Experimental and theoretical evidence did not seem to coincide satisfactorily. Furthermore, the absorption at 1718 cm^{-1} was observed in a like material that did not contain the crosslinker. Similar fluorocarbon compounds without the crosslinker and with larger than usual amounts of the phase-transfer catalyst, benzlytriphenylphosphonium chloride, prepared by Schmiegel[3,4] reached a state of cure about one-half as great as that of fully formulated compounds. However, these related materials showed a high compression set, likely indicating reduction in crosslinking density. Additionally, other researchers,[5] through wet analysis methodologies, established that similar compounds with and without the crosslinker produced on heating nearly equivalent amounts of hydrogen fluoride. All these observations led us to believe that a closer look at the solid-state chemistry of the system without the crosslinker was needed to fill some of the remaining ambiguities.

In this article, we attempted to explore in more detail than before the function of the accelerator and provide additional insight for the pathway leading to the final structural entity. We also try to provide some evidence on the makeup of a secondary network structure and its effect on the thermal stability of standard fluorocarbon compounds. In pur-

suit of these goals, SEC, FTIR, and ODR were used for the characterization of the solid-state structures.

EXPERIMENTAL

Materials

Fluoroelastomer A is a copolymer of vinylidene fluoride (VF$_2$) and hexafluoropropylene (HFP) obtained from the DuPont Co., with Mooney viscosity ML 1 + 10 at 121°C of 22, specific gravity of 1.82, fluorine present at 66% of the possible sites, and a VF$_2$/HFP mol ratio of 3.5. Fluoroelastomer B is a homopolymer consisting of VF$_2$ repeating units. It is supplied in the form of pellets or powder by Atochem North America, Inc., under the name Kynar 461. It has the following properties: white powder, melting point of 156–160°C, specific gravity of 1.76 at 23/23°C, and weight-average molecular weight ($\overline{M_w}$) of 534,000. Also, it can crystallize in at least three forms. Both the copolymer and Kynar resin were used in making compounds along with other ingredients used as received from the manufacturers. Magnesium oxide (Maglite D) and calcium hydroxide were obtained from C. P. Hall Co. At a 94% minimum purity, they serve primarily as acid acceptors and cure activators. Curative 20 is obtained in the form of pellets from a fluoroelastomer masterbatch containing 33% benzyltriphenyl-phosphonium chloride (BTPPCL) (DuPont). Curative 30, bisphenol AF (BPAF), is the crosslinker in the compound (DuPont).

Compounding and Molding

Compounding of fluoroelastomer A with curative 20 and the acid acceptors, i.e., MgO and Ca(OH)$_2$, was carried out on an 80 × 180 mm two-roll laboratory mill. The mill speed was 3.2 m/min and the gap between the rolls was 0.5 mm. The compounding ingredients were added slowly over a period of 1 min to the elastomer, which was previously banded on the roll mill. To provide a homogeneous mixture, the compound was cut continuously at the edges of the roll and moved to the center for 360 s. Compounds with and without the crosslinker, i.e., A-144 and A-148E, respectively, are given in Table I. Mixing the homopolymer (Kynar 461) with the ingredients was done on a ball mill. The powder form of Kynar 461 was ballmilled with the curative and the acid acceptors for 24 h. Before incorporating the accelerator, it was frozen with dry ice and pulverized. The compound based on Kynar 461 (A-158) is also shown in Table I.

Table I   Fluoroelastomer Formulations

Copolymer compound A-144

1. Fluoroelastomer A (VF$_2$/ HFP)	100.00	phr
2. Maglite D (MgO)	3.00	"
3. Calcium hydroxide (Ca(OH)$_2$)	6.00	"
4. Curative 20 (BTPPCL)	3.00	"
5. Curative 30 (BPAF)	4.00	"

Copolymer compound A-148E

1. Fluoroelastomer A (VF$_2$/ HFP)	100.00	phr
2. Maglite D (MgO)	3.00	"
3. Calcium hydroxide (Ca(OH)$_2$)	6.00	"
4. Curative 20 (BTPPCL)	3.00	"

Homopolymer compound A-158

1. Fluoroelastomer B (VF$_2$)	100.00	phr
2. Maglite D (MgO)	3.00	"
3. Calcium hydroxide (Ca(OH)$_2$)	8.00	"
4. Curative 20	8.40	"

Test specimens were prepared by curing compound A-148E at 177°C under 3.5 MPa pressure for specific time intervals. The material was freshened on a roll mill three or four times before molding to make sure that a homogeneous mixture was cross-linked. Similarly, compound A-158 was molded into specimens by quickly pressing the molding powder in the mold cavity and keeping it there for 3, 20, and 60 min. The specimens were bumped two to three times during the initial molding stage for preparing specimens without voids.

Oscillating Disk Rheometry (ODR)

The cure characteristics of the compounds were determined by a Monsanto rheometer, ODR 2000. The samples were freshened on a small mill before cure to assure a homogeneous mix. The rheometer rotor oscillates through a 3° arc at 1.66 Hz and exerts a shear strain on the sample as that sample cures.

Size-exclusion Chromatography (SEC)

The number- and weight-average molecular weights ($\overline{M}_n$ and $\overline{M}_w$) and molecular size distribution were determined by SEC using a Waters Model 150C ALC/GPC, equipped with a differential refractometer (ΔRI) and an automatic injector. The column set used consisted of four Ultrastyragel columns (30

cm $\times$ 7.8 mm i.d.) with permeability limits of 10^5, 10^4, 10^3, and 500 Å. The mobile phase was tetrahydrofuran (THF), flowing at 1.2 mL/min and 30°C. The relative sensitivity of the refractometer was set at 64. Injection volumes of 50 and 60 μL were used for duplicate SEC analyses. The column set was calibrated with commercially available polystyrene standards: peak molecular weights (M_p) ranging from 1.987 $\times$ 10^6 to 680. The average molecular weights cited are, therefore, relative to polystyrene standards.

Infrared Spectroscopic Measurements

Infrared spectra were obtained from 4000 to 400 cm^{-1} using a Mattson 5020 Fourier transform spectrometer that was equipped with a KBr beam splitter, a TGS detector, and a sample-background shuttle. Spectra were obtained with block coadding 64 interferograms at a mirror velocity of 0.6 cm/s and 4 cm^{-1} resolution. The Fourier transforming was accomplished with one order of zero filling. Samples were prepared as cast films on KBr plates using methylene chloride or acetonitrile to dissolve the polymer samples.

RESULTS AND DISCUSSION

Recent studies on compounds based on VF$_2$ copolymers (VF$_2$/HFP and VF$_2$/HFP/TFE) and the BPAF nucleophile resulted in determining the network structure that results from crosslinking.[7] Although the structural features of these materials were derived from solid-state data generated from compounds molded under industrial vulcanization conditions, uncertainties existed about the pathway, leading to the final structure and the identity of certain segments of the network. Unsaturation was present during curing as evidenced by the production of infrared intensity at 1718 cm^{-1} whether the compounds were prepared with or without the crosslinker (BPAF).

To provide some insight into these issues, the function of the accelerator was examined in compounds molded under similar conditions as the fully compounded materials. The corresponding amounts of ingredients, without the crosslinker, were combined with VF$_2$/HFP copolymer and mixed on a two-roll mill under conditions identical to those used for the preparation of the standard compound A-144. Details on compositions are shown in Table I.

Molded specimens were prepared after quenching the curing process in 1, 5, and 60 min. Representative

rheographs revealing the effects of accelerator, cure time, and temperature on torque are shown in Figures 1 and 2. As seen from Figure 1, compound A-148E, which does not contain the BPAF crosslinker, attained about 11% of the cure state of the fully compounded material A-144 when both are treated at 177°C. For the A-148E material, the ODR plots also show that 50% of cure develops the first 5 min and the cure curve does not level off in 60 min, indicating that the cure is still in progress.

The observed cure behavior of A-148E is not similar to that occurring in the standard material (A-144). Moreover, the type of bonds formed during crosslinking are unknown because the extent of reaction is relatively limited. The unsaturated moiety on the elastomer molecules indicated by solid-state infrared data in this report would probably be the reactive segment that normally forms the crosslinks. Thus, the crosslinks could be carbon–carbon bonds as proposed previously in earlier related experiments involving high-energy radiation of fluorocarbons.[9] A Diels–Alder reaction between two polymer chains would lead to a reduction of double bonds, a situation not evident from the solid-state infrared spectroscopic data. Continuous formation of double bonds would not allow observation of the proposed Diels–Alder reaction. The composition without the crosslinker, A-148E, presents not only a continuous increase in torque, but also an increase in color with cure time. For example, the samples represented in Table II (i.e., A_2, A_3, and A_4) show substantial color changes during the key stages of the cure process. The color changes most likely are indicative of an
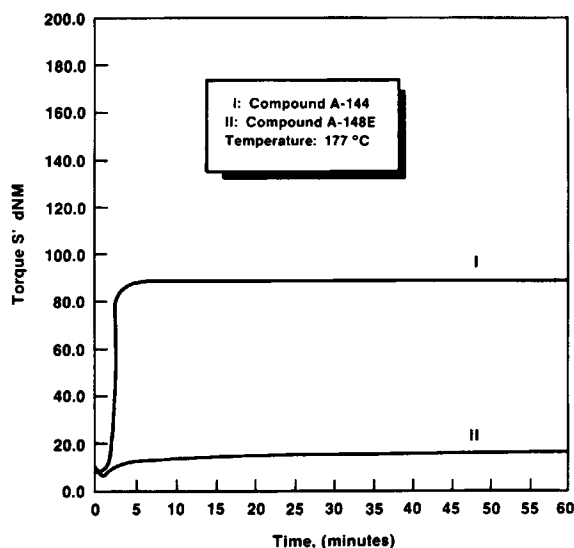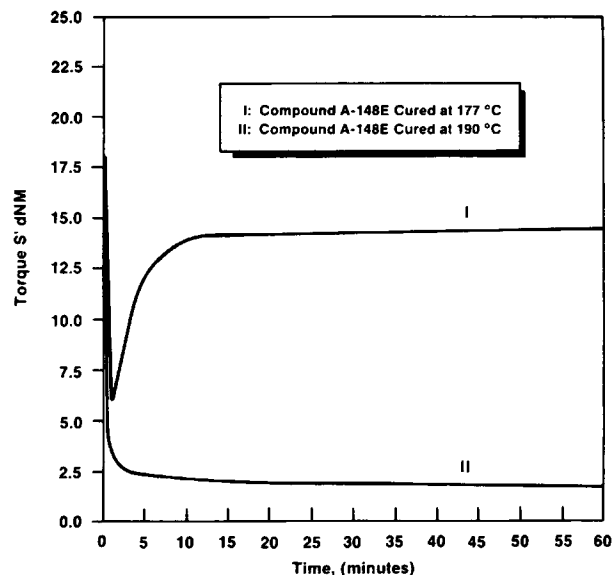

Figure 2 Effect of temperature on cure behavior of compound A-148E, which contains no crosslinker (note scale change from Fig. 1).

increasing conjugated unsaturation. The presence of such structures makes the occurrence of the Diels–Alder crosslinking chemistry quite possible, especially at these higher curing temperatures. However, no such reactions involving fluoroolefins have been documented in the open literature. Low reactivity of highly fluorinated dienes has been sited as a reason for the possible nonoccurrence of cycloadditions.[3] On the other hand, single fluoroolefinic segments of the polymer chains are considered very good nucleophiles. Also, cyclizations involving only conjugated fluoroolefin moieties cannot be ruled out.[10–12] Another possible crosslinking reaction based strictly on evidence from solid-state chemical events could involve an attack of fluoroolefinic segments by the nucleophilic fluoride ion analogous to the initiation step of anionic polymerization.[13] It would be oligomeric under optimum molding conditions with the destruction of the carbanion by hydrolysis or abstraction of a proton from an impurity. The propagation of a growing carbanion would also be limited by the fluoride ion elimination. It is apparent that a new type of crosslinking takes place in the absence of the crosslinker.

However, from Figure 2 (note scale change from Fig. 1), it is apparent that this secondary network does not form at 190°C or higher temperatures. It suggests that as these crosslinks form they are not stable at higher than normal molding conditions. The high compression set of compounds cured under standard conditions is in line with these findings.

Figure 1 Oscillating disk rheometer (ODR) traces for fluorocarbon compounds A-144 and A-148E at 177°C.

Although some of these crosslinks would be present in a standard compound, they would disappear during postcuring. Thus, the relatively stable phenolic crosslinks would be the only ones present in the final structure that comes in contact with the aggressive materials in automotive applications.

The copolymer (A_0), the unvulcanized material (A_1), and three molded samples of compound A-148E (A_{2-4}), taken after different times at the reaction temperature of 177°C, were analyzed by selective extraction and SEC to determine the types of reaction products produced during the vulcanization process. The five samples were extracted first with dichloromethane (DCM) and the residues were further subjected to a nonmixing, stepwise diffusive dissolution of the fluoroelastomer with acetonitrile (AN) at room temperature. The sample designations, sizes, and characteristics of the samples subjected to the extraction are summarized in Table II. The observed characteristics of these samples are presented in Table III.

DCM-extracted fractions obtained for fluoroelastomer-A samples A_0, A_1, A_2, A_3, and A_4 were 0.5, 1.1, 1.1, 0.9, and 0.9%, respectively, on the basis of the copolymer content, indicating only ca. 50% of the DCM extracts of compounded samples A_1–A_4 originated from the copolymer. Also, very little swelling occurred with DCM extraction of these samples.

Following the DCM extraction, the air-dried samples were subjected to the AN diffusive dissolution in three steps. First, a 3 mL portion of AN was added to each of the DCM-extracted residues of samples A_0–A_4 in 4 dram vials (15 × 45 mm) and the vials were sealed with PTFE-surfaced self-sealing septa assembled caps. The mixtures were kept at room temperature for 18 days and then 1 mL

Table II   Designations and Characteristics of Fluoroelastomer-A Samples for Solvent Extraction

Sample ID	Sample weight (mg)[a]	Compounding[b]	Molding time (min)[c]
A_0	195.7	None	None
A_1	244.0	A-148E	None
A_2	230.1	A-148E	1
A_3	260.7	A-148E	5
A_4	406.3	A-148E	60

[a] The elastomer content of samples A_1–A_4 is 89.3% (w/w).
[b] Without 4 phr of Curative 30 (BPAF).
[c] At 177°C under a pressure of 14,000 kg/ft³.

Table III   Variation of Compound (A-148E) Properties with Molding Time

I.d.	Molding Time (min)	Reaction (%)	Color	State
A_0	0	—	White	—
A_1	0	—	Light tan	—
A_2	1	Trace	Tan	Melt
A_3	5	> 50	Brown	Melt
A_4	60	< 100	Black	Elastic

each of the supernatant, clear solutions was carefully withdrawn with a 1000λ Lang Levy micropipet into a weighed 4 dram vial. AN was removed with a stream of nitrogen to obtain the amount of the AN-soluble elastomer fraction for each of the solutions. Second, as in the first step, the mixtures were allowed to stand for 8 days, after which time a gradual addition of another 2 mL portion of AN was made to each of the sample-residue vials (total AN volume: 4 mL). At this time, 2 mL was removed from each of the supernatant solutions and added to the corresponding original sample vials. Third, the nonmixing, AN-dissolution step 2 was repeated for the DCM-extracted sample residues.

The results of the AN-dissolution process are summarized in Table IV. The relatively constant weight percentages of cumulative AN-soluble fractions obtained at three dissolution steps for each elastomer samples indicate that the AN-soluble elastomer concentration in each of the supernatant layers is very close to an equilibrium concentration without any mixing. Therefore, the percentages of cumulative AN-soluble fractions obtained at the third step are taken as the solubility of samples A_0–A_4 in AN. The results are graphically shown in Figure 3, based on the fluoroelastomer-A content.

The gradual decrease in the AN-soluble fluoroelastomer-A components of samples A_0–A_3 probably indicates the increase in the network structures of compound A-148E samples. Thus, the solvent-extractable polymer chains are considered to be a precursor to form the network without crosslinking agents. The compound milling effect of the A-144 under a constant shearing (mill speed: 3.2 m/min; mill opening: 10 mm) on molecular weight was found to be relatively small by the shear degradation of the longer elastomer chains,[14] i.e., $M_r \geq 10^6$. However, under the present high-shear milling condition (mill speed: 3.2 m/min; mill opening: 0.5 mm), the network formation would dominate any types of the molecular weight degradation for sample A_0 of com-

Table IV   Acetonitrile Soluble Fractions from A-148E Obtained by Nonmixing, Stepwise Diffusive Dissolution, Following DCM Solvent Extraction

	Soln (mL)	Soln Taken (mL)	% Wt of Cumulative Soluble Fractions				
Step			A_0	A_1	A_2	A_3	A_4
1^a	3	1	72.5	76.2	69.2	69.9	56.4
2^b	2	2	70.2	70.7	65.5	70.0	53.7
3^c	2	2	79.2	75.6	73.2	72.6	55.9

[a] The maximum amount of AN-soluble fractions would be 33.33% of each elastomer sample weight.
[b] The maximum amount of AN-soluble fractions would be 66.67% of each elastomer sample weight.
[c] The maximum amount of AN-soluble fractions would be 83.33% of each elastomer sample weight.

pound A-148E, which are not compounded with the crosslinker BPAF.

The combined DCM extracts from samples A_0 (2.8 mg), A_1 (5.7 mg), and A_3 (5.8 mg) were dissolved in 2 mL each of THF and the mixtures were filtered through 0.5 μm Millex SR filters. The DCM extracts from samples A_1 and A_3 contained white THF-insoluble precipitates (ca. 50%). The filtered solutions were subjected to SEC analysis under the conditions described above. The THF-soluble portions of the DCM extracts contained only low molecular weight components (M_r = 300–800).

The solvent-stripped AN-soluble fractions of A-148E samples (35–39 mg) were redissolved in 3 mL each of THF. The THF solutions (ca. 2.5 mL) were filtered through 0.5 μm Millex SR filters. The results of SEC analysis are summarized in Table V together with the ΔRI area-response factors per mg of the AN-soluble fractions. The normalized SEC separation curves of the AN-soluble fractions are shown in Figure 4 for samples A_0–A_3 and in Figure 5 for samples A_3 and A_4. The progressive decrease in the refractive-index response factor per unit sample

weight from A_0 to A_3 suggests that there are chemical changes in the composition of AN-soluble fractions. The solubility of fluoroelastomer A in AN (79% for sample A_0) determined by the nonmixing, stepwise diffusive dissolution process is considerably lower than in tetrahydrofuran (THF, ca. 98%),[14] but the $\overline{M}_n$ and $\overline{M}_w$ of the AN- and THF-soluble fractions are very close to each other (i.e., $\le$ ±3%), suggesting that the average molecular weights of AN-soluble fractions could represent the majority of noncrosslinked fluoroelastomer A in the compounded samples A_1–A_4. However, it is possible that the crosslinked polymer chains formed during the compounding were not soluble in AN.

At approximately the molding time of 5 min at 177°C, both $\overline{M}_n$ and $\overline{M}_w$ had reached their maxima and then the values became lower under an extended molding time of 60 min for sample A_4. The cause of the average molecular weight lowering of noncrosslinked fluoroelastomer-A polymer chains (i.e., AN-soluble fractions) at the extended molding time would be a diminution in the forming of crosslinking

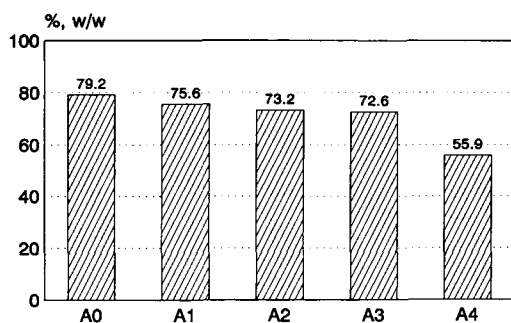**Acetonitrile Soluble Fluoroelasomer-A Components**

Figure 3   Solubility of fluoroelastomer samples A_0-A_4 in acetonitrile determined by a nonmixing, stepwise diffusion dissolution process.

Table V   Detector Responses and Average Molecular Weights of AN-Soluble Fluoroelastomer-A Fractions

Sample	ΔRI Response Per mg[a]	Av Mol Wt $\times$ 10^{-3} [b]		
		$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_w/\overline{M}_n$
A_0	418	81.8	180.3	2.20
A_1	368	87.4	194.8	2.23
A_2	340	96.7	220.2	2.28
A_3	236	91.9	221.1	2.41
A_4	235	73.4	195.1	2.66

[a] An average of two measurements (cf. Fig. 2).
[b] (SEC conditions) column: four Waters Ultrastyragel columns of 10^4, 10^6, 10^3, and 500 Å; flow rate: 1.2 mL/min; injection volumes: 50 and 60 μL; solvent: tetrahydrofuran; ΔRI detector sensitivity: 64 $\times$ 80 at 30°C.
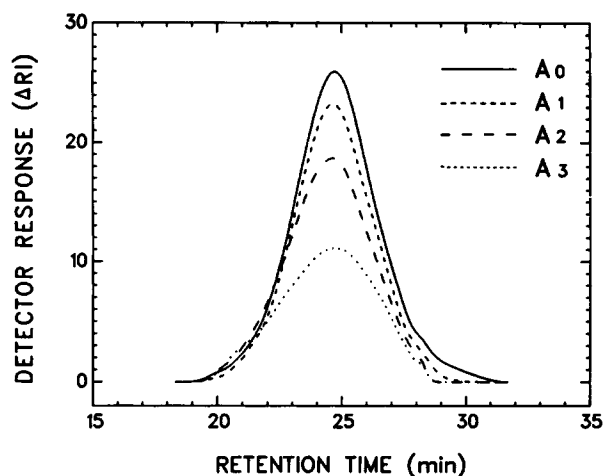
Figure 4 Normalized SEC separation curves of fluoroelastomer samples A_0-A_3 per unit weight (mg) detected by a differential refractometer (ΔRI).
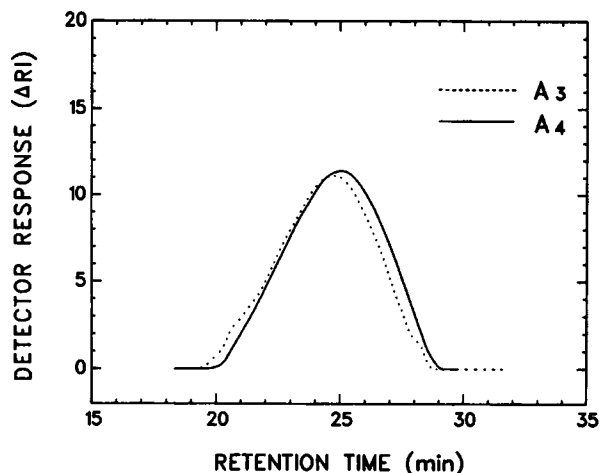

Figure 5 Comparison of normalized SEC separation curves of fluoroelastomer samples A_3 and A_4 per unit weight detected by ΔRI.

networks (i.e., diffusion control of the vulcanization). Also, the gradual increase in polydispersity ($\overline{M_w}/\overline{M_n}$, 2.2–2.7) suggests the possibility that both chain scission and network formation occurs at thermally initiated radical sites during the long molding time.

The infrared spectra of the material removed from the A-148E samples in the three step AN extraction above are presented in Figure 6. As seen in the A-144 sections in the earlier study,[7] the spectra obtained for the extracts indicate that there is no evidence of double bonds present prior to heating. The evidence of double-bond formation, as evident by the presence of the 1718 cm^{-1} band, is present even at 1 min exposure to 177°C. This feature continues to grow for the samples heated for 5 and 60 min and the presence of the weak shoulder at 3114 cm^{-1} is also apparent. Additionally, a shoulder is seen at 1680 cm^{-1}. As expected, the 1610 cm^{-1} band attributed to the formation of crosslinks by the BPAF additive are absent. Thus, the assignments made in the initial study are corroborated.

The first tangible link between the solution ^{19}F-NMR data of Schmiegel[3,4] for model reactions in solution and solid-state chemistry carried out in the absence of crosslinker at relevant vulcanization conditions can be taken from the spectra presented in Figure 6. The ^{19}F-NMR data was understood on the basis of the formation of the unsaturated moiety —C(CF$_3$)=CH— from base-sensitive sites by the loss of tertiary fluorine. Similarly, we observe for the extracts of compound A-148E changes in the infrared spectra at 1.5 min into the reaction consistent with the formation of the species

—CF=CH— at 1718 cm^{-1} from the species indicated above, which would have been present as the short-lived intermediate. Although the 1718 cm^{-1} band is the most prominent feature that grows
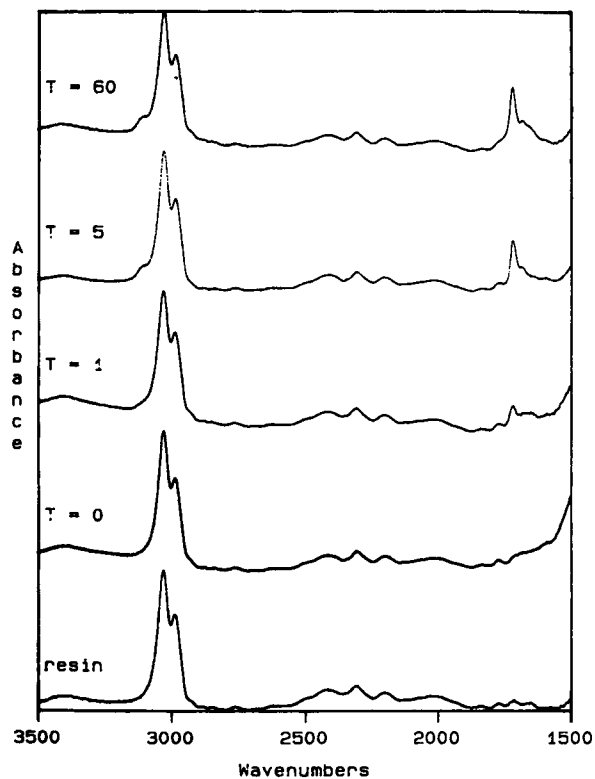

Figure 6 Midinfrared spectra from 3500 to 1500 cm^{-1} for samples of original fluoropolymer resin and compound A-148E that is either unreacted or removed after heating at 177°C for the indicated time in min.

in with time, there is a broad shoulder to the lower wavenumber side of this band that can be attributed to the $-C(CF_3)=CH-$ group and related isomeric species. As cure time increases, the 1718 cm^{-1} band grows as does the shoulder intensity. It is likely that this band-structure development is related to the equilibration of the contributing species in the reaction mix as has been suggested in Figure 7. By contrast, in the fully formulated compound, i.e., in the presence of the crosslinker, as studied in our earlier article, a broad peak was present from 1680 to 1720 cm^{-1} even after only 2.5 min of cure. This observation suggests that the 1718 cm^{-1} may be consumed in the formation of crosslinks and 1680 cm^{-1}-type structures. As curing progresses, the two main absorptions increase with the 1680 cm^{-1} band becoming relatively more pronounced compared to the current study where the crosslinker is absent.

Additionally, when the A-158 material compounded as in the A-148E material, no double-bond-associated features were seen in the spectra of the rubbery material formed or AN extracts even upon heating under pressure for 60 min. Commercial compounds made with propylene/TFE copolymer present spectra which show a strong feature at 1689 cm^{-1} and shoulder at 1720 cm^{-1} and no evidence of a 3114 cm^{-1} feature despite the presence of a strong $C=C$ stretching mode. We take this to suggest that the 1680 cm^{-1}-type feature in these fluoroelastomer systems is indicative of a double bond without any protons on either carbon, while the 1718 cm^{-1} feature, which is found in combination with an $sp2$ CH stretch at 3114 cm^{-1}, suggests the presence of a single proton on one of the carbons in the double bond formed.

Portions of the results presented herein complements previous reports from over the last two decades.[3-7] As an example, the work of Schmiegel constitutes a fundamental study of the broad aspects of fluorocarbon crosslinking with nucleophiles. He proposed reaction schemes for standard solid-state cures based on the analysis of ^{19}F-NMR solution spectra of model reaction products resulting from combination of fluorocarbons with hydroxylic bases or amines in aprotic solvents. Although one BPAF free compound was examined to establish changes during the induction period, infrared spectral observations were inadequate to clearly discern the detailed changes.[3] In contrast, this report focuses exclusively on the role of accelerator in the solid-state cures in fluorocarbon–nucleophilic reactions. The approach in the sample preparation and experimental design used here are unique and were chosen to provide insight on a crosslinker-free sys-

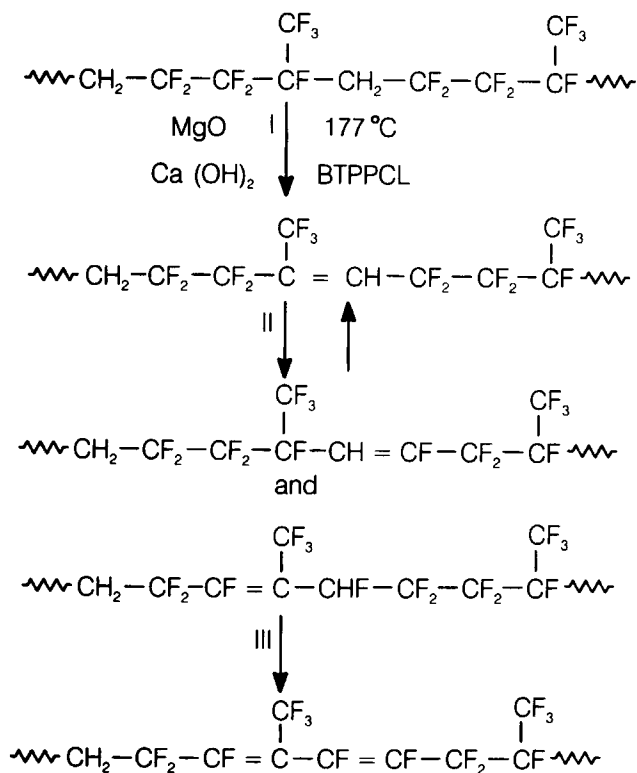## Reaction Scheme for Copolymer Compound A-148E

Figure 7 Reaction scheme for soluble fraction of copolymer compound A-148E.

tem cured under identical conditions to those used for the fully compounded material. These same techniques were considered to be inappropriate, for good reason at the time, or irrelevant for this type of work. Although our complementary results are in general agreement with previous efforts, the vision of this effort is wider than the earlier forays into pathway elucidation to the formation of a final network structure. The kinetic data derived from the system studied provide direct characterization of the fluoroolefinic segments of the polymer chains, describes the secondary network, and provides molecular weight parameters for part of the system. Further light has, thus, been shed on the cure schemes commonly utilized in industrial applications.

CONCLUSIONS

The function of an accelerator (BTPPCL) in the curing of VF_2/HFP copolymer by BPAF nucleophile has been examined. Infrared data of sections from

compounds containing no crosslinker and cured at 177°C indicate formation of unsaturation that absorbs in the infrared spectrum at 1718 cm^{-1}. Oscillating disc rheometry data derived from the same materials suggest that a secondary network is formed, likely due to reactions involving the unsaturated elastomer. Curing continues after 60 min at 177°C and color development is also a function of reaction time. However, this accelerator-induced network is not stable at higher curing temperatures such as 190°C. Thus, postcuring has the additional function of the elimination of the less stable linkages in the polymer network.

Specimens quenched during cure were also solvent-extracted. AN solubility of these materials varied with the extent of cure. SEC of the soluble portions shows a diminished detector response with cure time. This trend is believed to be related to the changes in structure and is in agreement with the infrared spectroscopic results. Furthermore, specimens with a cure state over 50% of the 60 min cure state show a shift to lower molecular weight. The higher molecular weight fractions may be contained in the crosslinked fraction, while the low molecular weight moieties may be formed by degradation.

Infrared spectra of the extracts show a regular increase in unsaturation as indicated by the increased intensity at 1718 cm^{-1}. From this result, it is concluded that the soluble fractions are, in general, very similar to the bulk composition obtained at different stages of reaction. Also, the intensity increase at 3114 cm^{-1} indicates the presence of $sp2$ CH groups. This evidence confirms the formation of CF$=$CH bonds, while the double bond absorbing at 1680 cm^{-1} remains as a minor shoulder throughout the cure process.

The devised nonmixing, stepwise diffusive dissolution process could be the only approach, however time-consuming, for the quantitative determination of the solvent-extractable fluoropolymer fractions in a milligram scale sample size of complicated compound mixtures, such as A-148E. The data obtained from the A-148E extracts provide an insight into the reaction pathway details similar to that based on earlier model solution reactions followed by ^{19}F-NMR. Furthermore, it also adds some distinct, new dimensions to the overall picture of the fluoroelastomer curing process conducted in the presence of nucleophiles.

REFERENCES

1. A. L. Moore, U.S. Pat. 4,694,045 (1987).
2. J. F. Smith and G. T. Perkins, *J. Appl. Polym. Sci.*, **5**, 460 (1961).
3. W. W. Schmiegel, *Kaut. Gummi Kunst.*, **31**, 137 (1978).
4. W. W. Schmiegel, *Angew. Macromol. Chem.*, **76/77**, 39 (1979).
5. P. Venkaleswarlu, R. A. Guenthner, R. E. Kolb, and T. A. Kestner, in *ACS Rubber Division Meeting*, Detroit, MI, 1989.
6. V. Arcella, G. Chiodini, N. DelFanti, and M. Pianca, in *ACS Rubber Division Meeting*, Detroit, MI, 1991.
7. A. N. Theodore and R. O. Carter III, *J. Appl. Polym. Sci.*, **49**, 1071 (1993).
8. D. Apotheker and P. J. Krustic, U.S. Pat. 4,035,586 (1977).
9. J. F. Smith, in *International Rubber Conference*, Washington, DC, 1959.
10. M. Prober and W. T. Miller, Jr., *J. Am. Chem. Soc.*, **71**, 598 (1949).
11. R. W. Schlag and W. B. Peatman, *J. Am. Chem. Soc.*, **86**, 1676 (1964).
12. I. L. Karle, J. Karle, T. B. Owen, R. W. Broge, A. H. Fox, and J. L. Hoard, *J. Am. Chem. Soc.*, **86**, 2523 (1964).
13. W. Brimskill, W. T. Flowers, R. Gregory, and R. N. Haszeldine, *Chem. Commun.*, **1970**, 1444 (1970).
14. M. Zinbo and A. N. Theodore, *I&EC Res.*, **33**, 1017–1021 (1994).