

The Thermal Oxidative Degradation of an Ethylene-Tetrafluoroethylene-Copolymer-Based Electrical Wire Insulation

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SYNOPSIS

A multidisciplinary spectroscopic evaluation of a commercial wire insulation based on a cross-linked copolymer of ethylene and tetrafluoroethylene (X-ETFE) was conducted to determine the chemical changes taking place during thermal aging. These studies provided insight into the roles of the various additives, such as triallylisocyanurate (TAIC) and antimony oxide, in the formulated X-ETFE insulation. During irradiation processing, a large fraction of the TAIC is converted to a cross-linked isocyanurate moiety; the unconverted TAIC is released during aging. Thermal aging of the X-ETFE wire insulations was performed in air at 200°C for up to 5 months and resulted in oxidation of the base ETFE, loss of unreacted TAIC, and a small amount of dehydrofluorination. The antimony oxide serves the multiple roles of flame retardant and scavenger for the pyrolytically generated hydrogen fluoride.

INTRODUCTION

Degradation of thermoplastic polymers is a complex process,¹⁻⁵ characterized by chemical and/or physical changes (aging). Chemical changes include such diverse reactions as oxidation, main-chain bond cleavage, and cross-linking. Loss of additives can result in bulk property changes that are subtle and difficult to measure within the lifetime of a laboratory experiment; however, these changes are important in the system design stages. An incomplete understanding of aging mechanisms can lead to costly errors or, in extreme cases, to unforeseen and catastrophic failure.

The irradiated copolymer of ethylene and tetrafluoroethylene, henceforth X-ETFE, is the polymeric base for a new class of high-temperature, long-lived electrical insulation material. Operating con-

ditions require that the fundamental mechanical and electrical properties of this insulation remain unchanged during prolonged periods at elevated temperatures. cursory visual observations indicate that the X-ETFE-based insulation systems may not satisfy these requirements. The insulation turns yellow after a few days at 220°C in air, and after 2 months aging, a brown color develops that continues to darken with further aging. Moreover, X-ETFE insulations contain complex, proprietary formulations of flame retardants, plasticizers, and cross-linking agents. Such complex systems are subject to large variances in formulation and processing and, subsequently, in their chemical and physical properties. Previous reports on the thermal stability of fluoropolymers indicate that degradation at elevated temperatures is dependent on the degree of cross-linking and the amount of additives present.⁶⁻¹⁰ Although triallylisocyanurate (TAIC) and antimony oxide are prominent components in some commercial wire insulations,¹¹ the role these materials play, and their fate during processing and aging, has not been reported.

To predict the long-term stability of these systems, a better understanding of the chemical changes

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that occur during thermal aging is needed. To develop this understanding, we initiated a multidisciplinary spectroscopic evaluation of X-ETFE systems and report the results from one commercial wire insulation. Chemical changes that occurred during thermal aging are identified and insight is provided into the roles the TAIC and Sb_2O_3 additives play in the aging process.

EXPERIMENTAL

Neat unirradiated ETFE resins were used to provide base-line information concerning the thermal aging characteristics of the base polymer in the commercial wire system. All samples were aged in air inside an oven regulated at $200 \pm 2^\circ\text{C}$. Aging times were varied from 9 days to several months. Several types of wire constructions were investigated: 22-gauge dual wall primary wire (mil. spec, M22759/33-22) and 26-gauge single-wall multistrand primary wire (mil. spec, M22759/33-26-9). The typical wire construction is irradiated to a total dose of approximately 8–10 Mrad.

Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed with a DuPont 900 series thermal analyzer and a DuPont 9900 computer. Samples were heated linearly at $\sim 10^\circ\text{C}/\text{min}$ with a nitrogen purge rate of 25 mL/min.

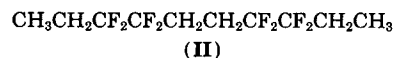
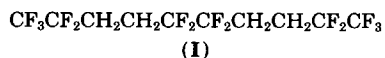
Evolved gas analysis using mass spectrometry (EGAMS) was performed with a Vacuum Generators ZAB-3F-HF instrument (consisting of a magnetic sector, electrostatic sector, and magnetic sector in sequence) with electron impact (EI) ionization. Initial survey runs were performed using the first two sectors (double focusing) with a resolving power, $M/\Delta M$, of ~ 2000 . The solids probe for the VG mass spectrometer, equipped with a resistance heater and thermocouple, was used for temperature measurement and control. While the mass spectrometer was continuously scanned at 10 s/decade of mass (from 800 to 10 daltons), the solids probe was heated from 100 to 550°C at a linear rate of $10^\circ\text{C}/\text{min}$. At the conclusion of the heating process, the solids probe temperature was held at 550°C for approximately 30 min.

The evolution of a particular compound can be monitored by plotting the intensity of a characteristic ion as a function of scan number. Such plots are called extracted ion current profiles. In addition, the complete mass spectrum can be examined at any temperature to obtain information about the mix-

ture of materials being evolved. When more information is required about an ion or ion fragment, a variety of tandem mass spectrometric techniques can be applied with the Vacuum Generators ZAB-3F-HF instrument. These techniques provide parent, daughter, and neutral-loss spectra from collision-induced dissociation (CID) using high-energy (~ 8 keV) helium ions. The benefits of tandem mass spectrometry are described with details of the experiments in Ref. 12. More information on the EGAMS technique can be found in reviews by Langer¹³ or Morelli.¹⁴

X-ETFE-based wire insulations were analyzed in two forms: (1) a small (~ 1 mg) piece cut from the wire construction, and (2) a small intact piece of wire containing the conductor. Inclusion of the conductor did not effect the mass spectra obtained from the insulation segment.

Reference mass spectra of tetradecafluorodecane (I) and octafluorodecane (II)¹⁵ were obtained from the NIH/EPA mass spectral data base. One ion of particular interest noted in the spectra from both (I) and (II) was the m/z 147 ion, corresponding to $(\text{CF}_3\text{CF}_2\text{CH}_2\text{CH}_2)^+$, which Santoro and Piccardi¹⁶ noted appears with almost equal intensity in both I and II.



Furthermore, we have observed that m/z 147 is always a strong signal in neat ETFE systems regardless of pretreatment, processing, or pyrolysis temperature. The m/z 147 ion has been used successfully as a reference signal in previous mass spectrometric investigations¹⁷ and, consequently, serves as such in this work.

Solid-state ^{13}C -NMR spectra were obtained on a Bruker MSL-300 NMR spectrometer. The electrical wire insulation was cut into small pieces, combined with sulfur powder, and packed into a magic-angle spinning (MAS) rotor. Cross-polarization MAS (CP/MAS) ^{13}C -NMR spectra^{18,19} were obtained at room temperature by using a hydrogen-carbon contact time of 5 ms and 71 kHz ^1H decoupling. The MAS rates of 4–6 kHz were not sufficient to completely remove ^{13}C – ^{19}F dipolar broadening, especially in the tetrafluoroethylene segments. A 5 s repetition time was used, and 500–15,000 scans were accumulated for each spectrum.

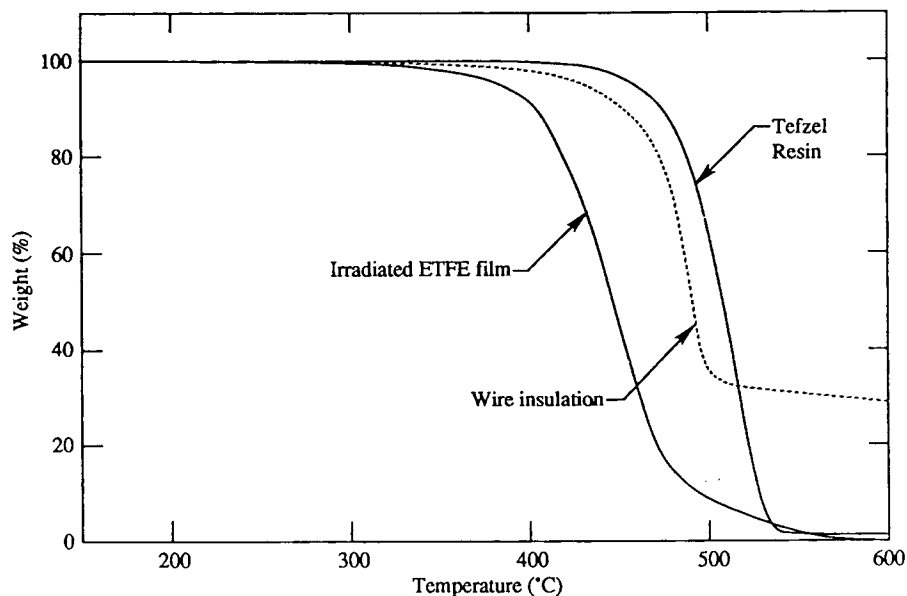


Figure 1 TGA results from neat Tefzel resin, ETFE film (irradiated with 29 Mrad of γ -irradiation), and a commercial wire insulation. N_2 purge rate 25 mL/min. Heating profile $10^\circ C/min$.

Infrared analysis was conducted using a Nicolet 170SX FTIR with HgCdTe detector. The spectral region between 4000 and 400 cm^{-1} was monitored. All samples were ground with KBr and analyzed as pellets. Care was taken to minimize water content in the KBr pellet. Occasional absorption bands from water contamination were observed but were not detrimental to the analysis.

RESULTS

Thermal analysis methods were used to supplement the EGAMS studies with regard to temperature-time profiles and particularly for quantifying the temperature at which decompositions occur. The thermogravimetric analyses (TGA) of neat virgin ETFE resin (DuPont Tefzel), an ETFE film irradiated to

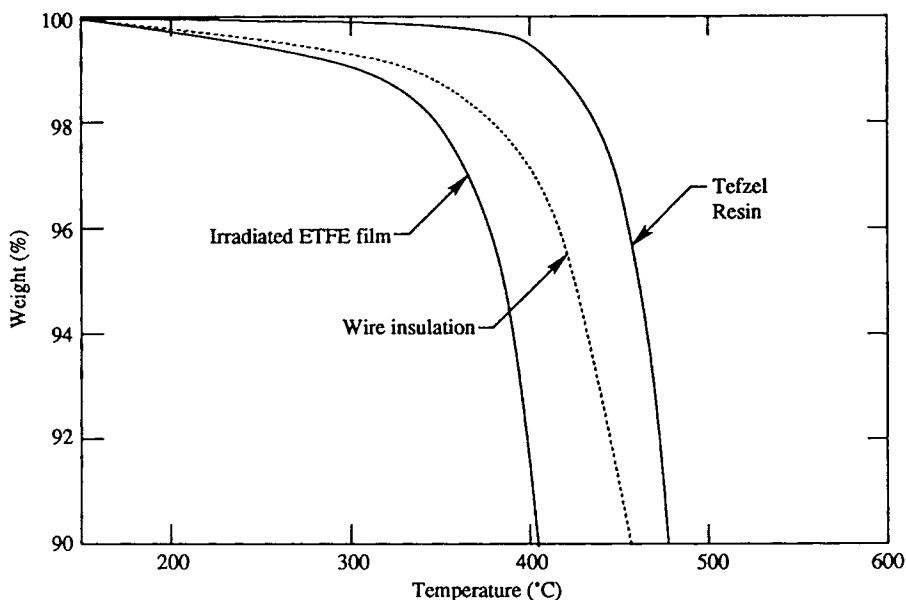


Figure 2 Expanded view of Figure 1 showing first 10% of weight loss.

a total dose of 29 Mrad (γ -rays ^{60}Co), and a typical commercial wire insulation containing TAIC and antimony oxide are shown in Figures 1 and 2. The entire weight loss curve is shown in Figure 1, whereas the first 10% weight loss (i.e., from 100% to 90%) is shown in Figure 2. Pure ETFE shows greater thermal stability at elevated temperatures than does either irradiated ETFE or the commercial insulation; however, thermal stability is only one property of interest in an insulation. The mechanical properties of the irradiated film and commercial insulation are superior. In the ETFE system, irradiation improves the mechanical properties at the cost of thermal stability.

The results from DSC analyses of neat Tefzel resin and the commercial wire insulation are shown in Figure 3. Tefzel has the highest and sharpest melting point, suggesting that it has the most ordered morphology of the samples studied.

Commercial X-ETFE wire insulations from different vendors, although meeting a specific military specification, are quite complex and different. Furthermore, we have found that X-ETFE insulations from the same vendor varied markedly in many properties when they were specifically formulated for different purposes. Nevertheless, our experience has shown that two additives, triallylisocyanurate (TAIC) and antimony oxide (Sb_2O_3), are prevalent in several formulations. EGAMS studies can detect

the presence of these compounds and, additionally, several species relevant to the pyrolytic degradation of these insulations. Examples of the degradation products are hydrogen fluoride (HF) and the various fragments from X-ETFE.

Figure 4(a-c) shows the mass spectra of the three major components in the wire. Figure 4(a) shows the EGAMS positive ion spectrum from the insulation when the solids probe was between 400°C and 500°C and corresponds to the pyrolysis-MS spectrum of neat Tefzel (ETFE) resin. The spectrum shown in Figure 4(b) is the result of subtracting the spectrum in Figure 4(a) from the spectra obtained from the insulation with the solids probe at $\sim 200^\circ\text{C}$. This spectrum is identical to that observed from neat triallylisocyanurate. The spectrum shown in Figure 4(c) is the result of subtracting the spectrum in Figure 4(a) from the spectrum obtained while the solids probe was at 550°C. The ions shown in Figure 4(c) are from Sb_2O_3 . An ion cluster at m/z 159 and attributed to SbF_2 was also noted. The observed isotopic distribution of the m/z 159 cluster and that expected for SbF_2 is shown in Table I.

The total ion current profiles obtained from unaged and aged neat Tefzel resin are shown Figure 5; both contain two maxima. No difference was observed in the mass spectra of the species evolved at these two maxima, nor were any differences in speciation observed when comparing the spectra ob-

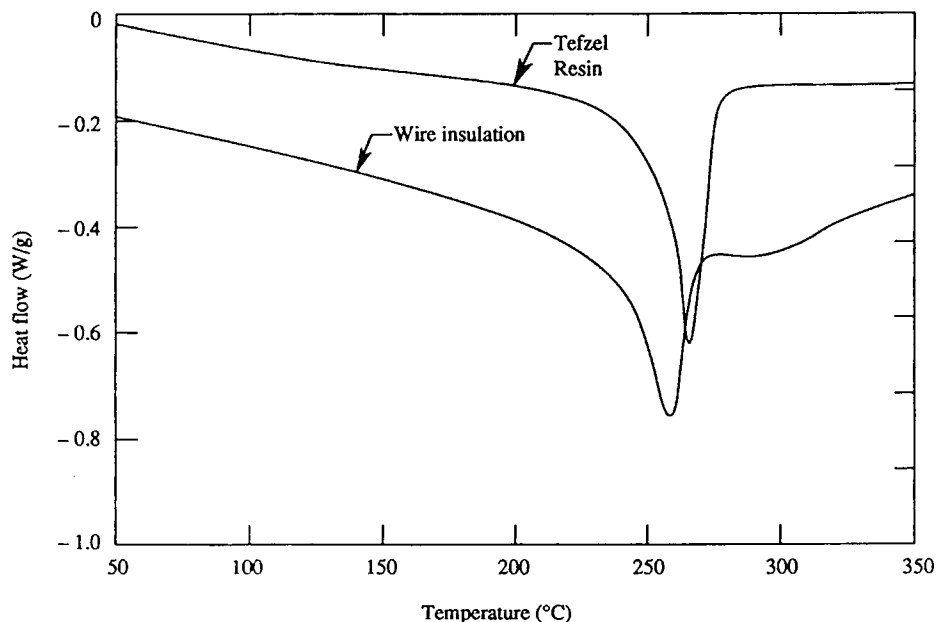


Figure 3 DSC results from neat Tefzel resin and a commercial wire insulation. N_2 purge rate 25 mL/min. Heating profile $10^\circ\text{C}/\text{min}$.

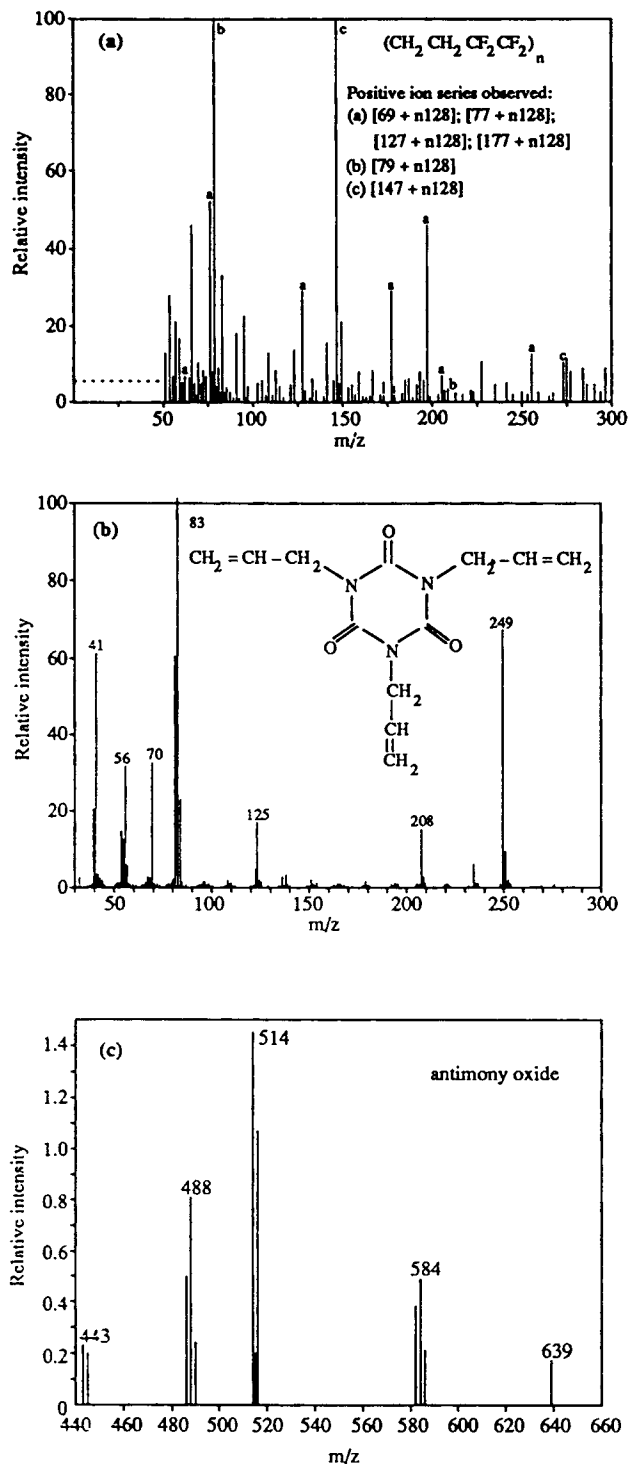


Figure 4 EGAMS spectra of major components present in commercial wire insulation. (a) Typical spectrum observed from wire insulation while solids probe is between 400 and 500°C. (b) Obtained by subtracting (a) from signal observed while solids probe was at ~ 200°C. (c) Obtained by subtracting (b) from signal observed while solids probe was at ~ 550°C.

Table I Isotopic Distribution of SbF_2

m/z (Observed)	m/z (Expected)	Relative Intensity (Observed)	Relative Intensity (Expected)
159.9	159.9	100.0	100.0
160.9	160.9	75.0	74.5

served at maxima from aged and unaged resins, although the low-temperature maximum was less intense in the aged resin than in the unaged resin. The spectra of ETFE shown in Figure 4 (a) is typical of those obtained from neat ETFE at both maxima.

The changes that occurred in the EGAMS profiles following thermal oxidative aging are summarized in Figures 6 (a-f). The amount of material released at low temperatures, i.e., less than 200°C, from the as-received samples is significantly more than that released from the aged samples; however, the type of species observed at ~ 550°C in aged and as-received product are the same. For each species [Figs. (b-f)], a decreased intensity is observed below 200°C, which suggests that the species are present as indigenous volatile compounds perhaps produced during fabrication; a process which requires that the insulation be heated above its melting point.

Figure 7 shows the CP/MAS ^{13}C -NMR spectra of unaged Tefzel (a), aged Tefzel (b), as-received insulation (c), and aged insulation (d). The aged systems were subjected to thermal oxidative aging in air at 200°C for approximately 6 months. Figure 7 (e) shows the high-resolution ^{13}C -NMR spectrum of a 5% w/w solution of TAIC in acetone- d_6 . Assignments of resonances from TAIC are shown along the bottom axis of Figure 7. The primary features of all the spectra are the resonances observed at 23 ppm for $-\text{CF}_2\text{C}^*\text{H}_2\text{CH}_2-$ and 115 ppm for $-\text{CH}_2\text{C}^*\text{F}_2\text{CF}_2-$. Spinning sidebands, indicated by s in Figure 7, are prominent about the $-\text{CH}_2\text{C}^*\text{F}_2\text{CF}_2-$ resonance because of the ^{19}F - ^{13}C dipolar interactions.

During aging, a new resonance is observed in both materials at ~ 90 ppm. We tentatively assign this resonance to the fluoromethine moiety (shown in Fig. 7), a product likely to form by dehydrofluorination between adjacent polymer chains, i.e., cross-linking. In the insulation, the intensity of the TAIC resonances become noticeably reduced during aging; only the carbonyl resonance at 149 ppm is clearly identifiable after aging.

The IR spectra of as-received and aged insulation

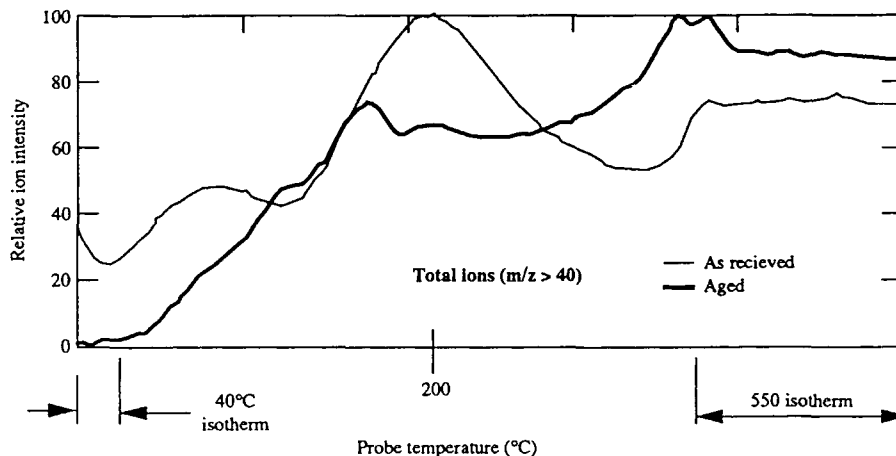
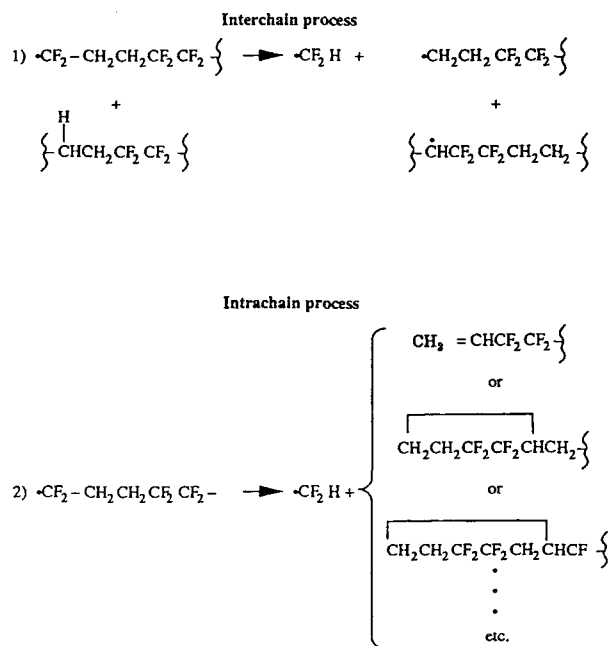


Figure 5 Total ion current profiles from aged and unaged neat Tefzel resin. Aged resin was subjected to 200°C in air for 9 days.

are shown in Figure 8 and can be interpreted with the aid of data published on the IR spectra of neat Tefzel. The carbonyl stretch at 1700 cm^{-1} of the unaged insulation is due to TAIC.²⁰ The broader OH overtone at 1600 cm^{-1} in the unaged insulation was due to water contamination in the KBr pellet. After aging, the 1800 to 1400 cm^{-1} region of the spectrum changed dramatically, while the remaining portions of the spectrum were essentially identical. In particular, the carbonyl stretch at 1700 cm^{-1} is reduced and broadened. Work with neat ETFE films¹⁷ indicated that ETFE oxidizes during thermal aging to produce carbonyl-containing species. These species result in IR spectra showing a carbonyl stretch at 1760 cm^{-1} ; furthermore, the band is much broader than the carbonyl stretch observed for triallylisocyanurate. Thus, the IR spectral changes observed in the region between 1650 and 1800 cm^{-1} following aging arise from two separate species: the carbonyl stretch from the unreacted TAIC, and another from the carbonyl species produced during thermal oxidation of the ETFE polymer network. The remaining features of the IR spectra from as-received and aged wire insulations are similar to that observed in the neat ETFE systems.^{17,20-24}

DISCUSSION

In another study, hydrogen and fluorine migration were found to occur during pyrolysis of irradiated ETFE, probably via a combination of interchain and intrachain processes¹⁷:



Low molecular weight fluorocarbon oligomers containing 4 to 16 carbons are produced by random chain scission reactions; HF is directly produced by dehydrofluorination. The HF elimination, observed by EGAMS [see Fig. 6(b) and Ref. 17], occurs at a lower temperature than that required to produce the low molecular weight oligomers (250°C), suggesting that different degradation processes occur above and below 250°C. This observation supports previously documented concerns that HF elimination reactions are a potentially serious problem when fluorinated polymers are used at temperatures approaching 200°C.²⁵

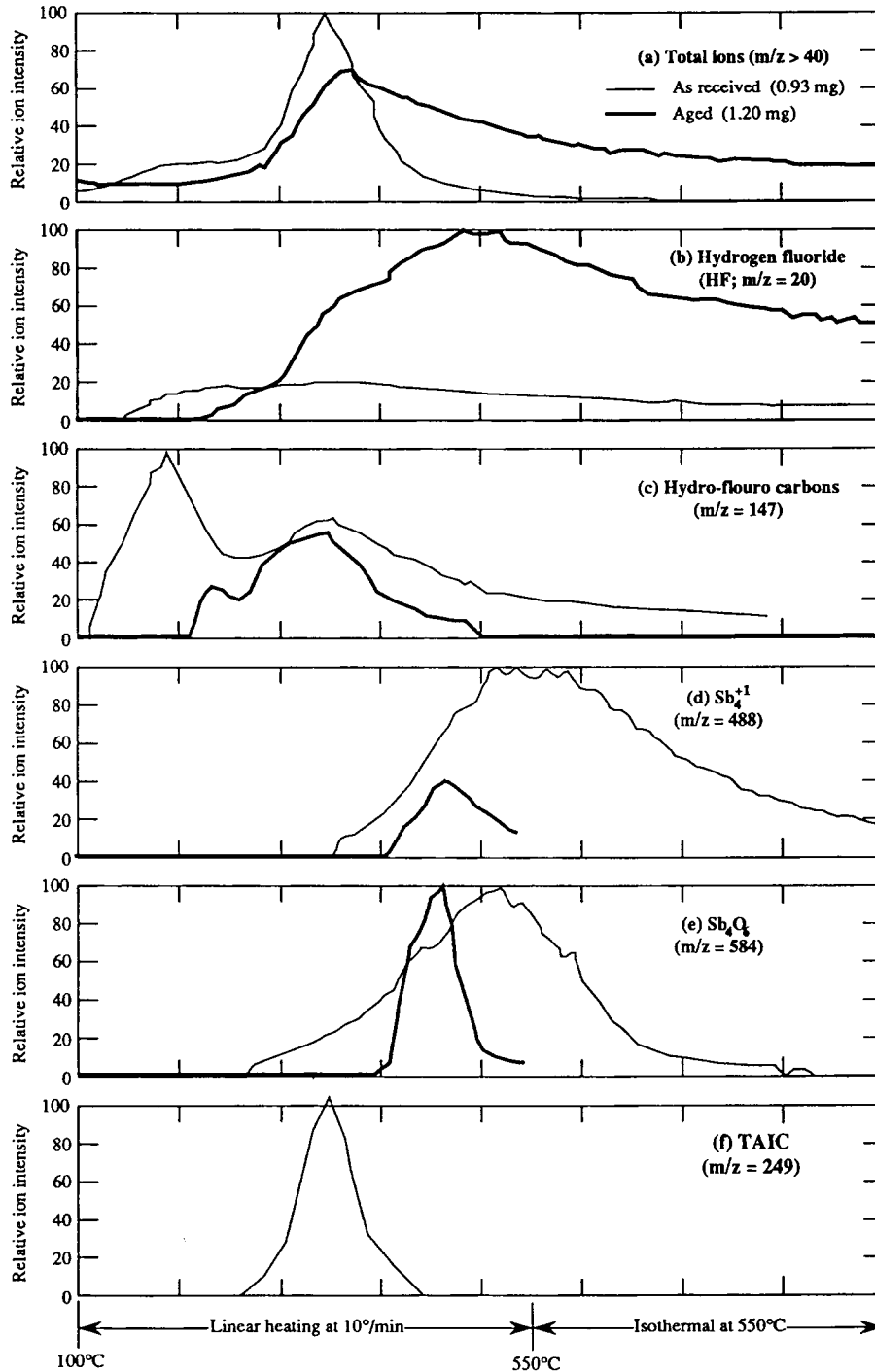


Figure 6 EGAMS ion profiles from aged and unaged commercial wire insulations. Aged wires were subjected to 200°C in air for 9 days.

A method to quantify the HF produced during pyrolytic decomposition of polymers, such as ETFE, was described previously.²⁶ In the quantitative study by Morelli et al.,²⁶ the wire that yielded the least

amount of HF contained Sb_2O_3 . We continue to observe that wire insulations containing antimony oxides yield smaller amounts of HF than do those without antimony oxide and that these wires show

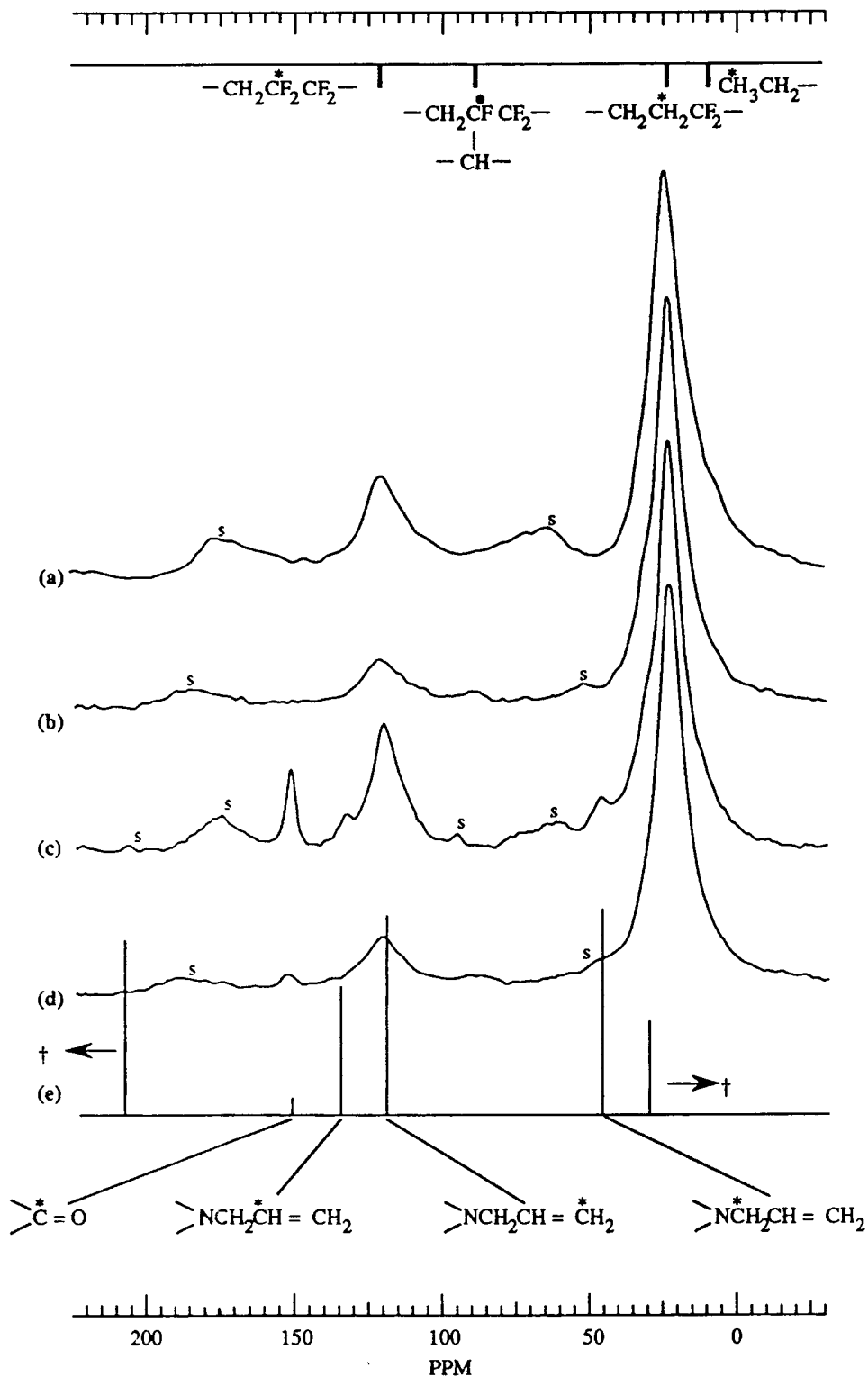


Figure 7 CP/MAS ^{13}C -NMR spectra of unaged (a) and aged (b) Tefzel resin, as-received (c) and aged (d) wire insulation. Aged systems were subjected to 200°C in air for 6 months. (e) The high-resolution ^{13}C -NMR spectrum of 5% w/w TAIC in acetone- d_6 .

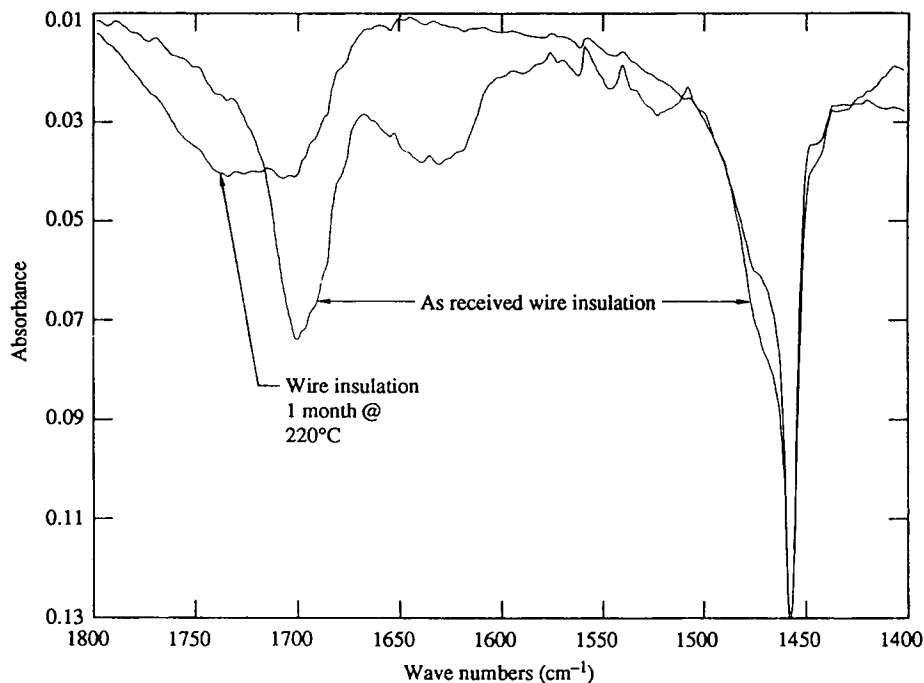


Figure 8 IR spectra (1800 and 1390 cm^{-1}) of as-received and aged wire insulations between aged insulations were subjected to 200°C in air for 1 month.

signals due to SbF_2^+ . The halogen-synergism of antimony trioxide is well documented¹¹ as the mechanism facilitating flame retardation in polymer formulations containing the oxide. The antimony fluoride species observed during EGAMS experiments results from the reaction of HF with Sb_2O_3 , i.e.,



As HF is formed during thermal degradation, much of it rapidly reacts with the Sb_2O_3 , reducing the amount of HF evolved.

The amount of TAIC present in the wire insulations was sufficient to be detected by IR, NMR, and EGAMS. TAIC can be used as a plasticizer and/or a cross-linking agent during irradiative cross-linking processing.²⁷⁻³⁷ After aging, EGAMS shows no evolution of TAIC [Fig. 6(f)]. NMR analysis indicates that the carbonyl from the carbamide moiety is still present, and IR confirms the presence of carbonyl. The changes observed in the EGAMS, NMR, and IR spectra indicate that the carbonyl moiety is bound to the ETFE backbone, as illustrated in Figure 9. Variable contact time NMR experiments indicate that the allyl carbons are reduced significantly with aging as compared to the carbonyl carbons; furthermore, EGAMS suggest that the TAIC is unreactive within the base polymer at

~ 200°C during the time scale of the analysis since no adducts between TAIC and ETFE were detected. Thus, unreacted residual TAIC coexists with the cross-linked isocyanurate species in as-received wire insulation. Upon aging at 200°C, the residual unreacted TAIC evolves, leaving only the cross-linked isocyanurate species. Depending upon the particular formulation, TAIC can be used as a plasticizer; hence, the loss of residual TAIC combined with the thermal oxidation of the ETFE¹⁷ may produce a stiffer, more brittle insulation.

CONCLUSIONS

X-ETFE wire insulations require complex formulation procedures to produce systems with the desired electrical, mechanical, chemical, and visual properties necessary for successful commercial application. During processing, a variety of materials are produced in addition to those intentionally added. Formation and irradiation of ETFE resin produces low molecular weight oligomers that are trapped within the matrix of the insulation. These materials are gradually lost during the lifetime of the system; at 200°C (in air), they evolve in less than 24 h.

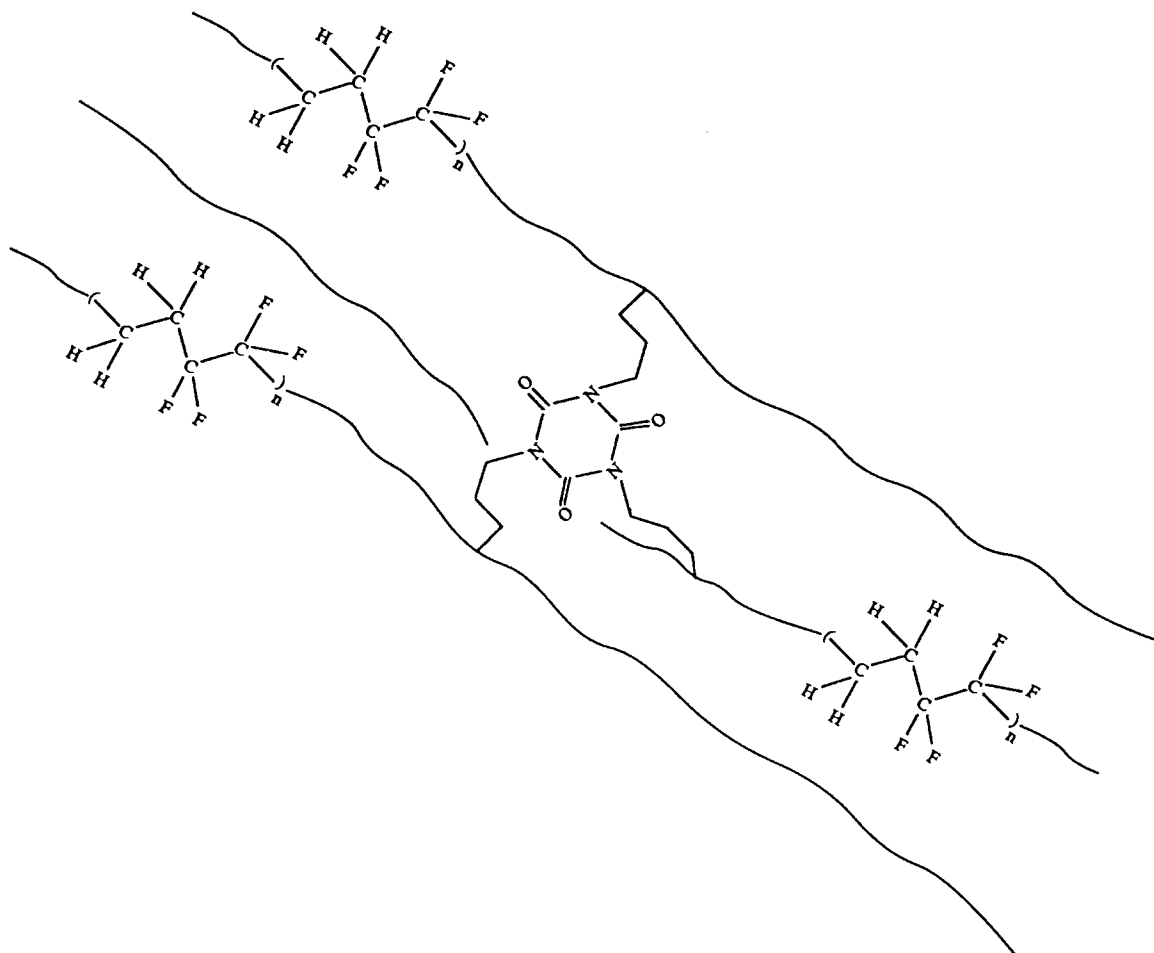


Figure 9 Hypothetical adduct of TAIC cross-linked within the network of ETFE.

Irradiation cross-linking is used to improve the high-temperature mechanical properties of the base ETFE resin. During irradiation processing, TAIC is converted to a cross-linked isocyanurate species, although a small amount of residual unreacted TAIC remains. During thermal aging of the X-ETFE wire insulations in air at 200°C, a variety of chemical changes including the oxidation of the base ETFE insulation, loss of uncross-linked TAIC, and dehydrofluorination were observed. These chemical changes also include an increase in the degree of cross-linking as determined by the NMR experiments employed in this study. In addition, these chemical changes have measurable effects on the visual and mechanical properties of the wire insulation; therefore, we believe that these chemical changes may impact the useful lifetime of the insulation. Future work will attempt to quantitatively correlate the changes in mechanical properties with the chemical changes observed. We have found that many of the commercial X-ETFE-based insulations

examined to date contain detectable amounts of TAIC and Sb_2O_3 ; the information gained in this study should be applicable to understanding the chemical changes that occur during thermal aging in any X-ETFE-based system.

REFERENCES

1. S. L. Madorsky, *Thermal Degradation of Organic Polymer*, Interscience, New York, 1964.
2. H. H. G. Jellinek, *Aspects of Degradation and Stabilization of Polymers*, Elsevier, New York, 1978.
3. N. M. Emanuel and A. L. Buchachenko, *Chemical Physics of Polymer Degradation and Stabilization*, VNU Science Press, Utrecht, Netherlands, 1987.
4. R. T. Conley, *Thermal Stability of Polymers*, Marcel Dekker, New York, 1970.
5. N. Grassie, *Developments in Polymer Degradation*, Elsevier, New York, 1985.
6. J. M. Cox, B. A. Wright, and W. W. Wright, *J. Polym. Sci.*, **8**, 2935-2950 (1964).

7. J. M. Cox, B. A. Wright, and W. W. Wright, *J. Polym. Sci.*, **8**, 2951-2961 (1964).
8. S. Barron, in Fire Retardation, *Proceedings of the International Symposium on Flammability*, 1978, pp. 1-14.
9. L. D. Bustard, J. Chenion, F. Carlin, C. Alba, G. Gaussens, and M. LeMeur, in *Proceedings of the U.S. Nuclear Regulation Commission, Water Reactor Safety Research*, 12th International Meeting, NURE/CP-0057-V5, U.S. Nuclear Regulating Commission, 1984, pp. 401-425.
10. R. L. Clough, K. T. Gillen, and C. A. Quintana, *J. Polym. Sci. Polym. Chem. Ed.*, **23**, 359-377 (1985).
11. R. Gachter and H. Muller, *Plastics Additives Handbook*, Hanser, New York, 1985.
12. F. W. McLafferty, *Tandem Mass Spectrometry*, Wiley, New York, 1983.
13. H. G. Langer, *Thermochim. Acta*, **100**, 187-202 (1986).
14. J. J. Morelli, *J. Anal. Appl. Pyrolys.*, to appear.
15. S. R. Heller and G. W. A. Milne, EPA/NIH Mass Spectral Data Base, National Bureau of Standards, Washington, DC, 1978.
16. E. Santoro and P. Piccardi, *Organ. Mass Spectromet.*, **7**, 123-131 (1973).
17. J. J. Morelli and T. C. Sandreczki, *J. Am. Chem. Soc.*, to appear.
18. A. Pines, M. G. Gibby, and J. S. Waugh, *J. Chem. Phys.*, **59**, 569 (1973).
19. J. Schaefer and E. O. Stejskal, *J. Am. Chem. Soc.*, **98**, 1031 (1976).
20. C. J. Pouchert, *The Aldrich Library of Infrared Spectra*, Aldrich Chemical Company, Milwaukee, WI, 1981.
21. H. J. Kretzschmar, D. Gross, and J. Kelm, *Kunststoffe*, **69**, 154-157 (1979).
22. L. I. Tarutina, *Zh. Prikl. Spektrosk.*, **8**(4), 653-656 (1968).
23. H. Orth, *Makromol. Chem.*, **141**, 69-75 (1986).
24. L. N. Pirozhnaya and L. I. Tarutina, *Zh. Prikl. Spektrosk.*, **34**(5), 862-865 (1981).
25. W. W. Wright, in *Developments in Polymer Degradation-6*, N. Grassie, Ed., Elsevier, New York, 1985.
26. J. J. Morelli, M. A. Grayson, and C. J. Wolf, *Anal. Chem.*, **61**, 802-805 (1989).
27. S. C. Zingheim, Ger. Pat. 2,825,995. (1979) (to Raychem Corp.); *Chem. Abstr.*, **90**, 105043c (1979).
28. Z. Ranogajec and M. Baric, *Polimeri (Zagreb)*, **5**, 233-234 (1984).
29. K. Shingyochi, S. Kashiwazaki, Y. Ando, and M. Yamazaki, Jpn. Pat. 60/137,953,A2 (1985) *Chem. Abstr.*, **104**, 6841n (1985).
30. K. Shingyochi, S. Kashiwazaki, Y. Ando, and M. Yamazaki, Jpn. Pat. 60/137,918,A2 (1985) (to Hitachi Cable, Ltd.); *Chem. Abstr.*, **104**, 6664g (1985).
31. K. Shingyochi, S. Kashiwazaki, Y. Ando, and M. Yamazaki, Jpn. Pat. 60/137,952,A2 (1985) (to Hitachi Cable, Ltd.); *Chem. Abstr.*, **104**, 6661d (1985).
32. K. Shingyochi, S. Kashiwazaki, Y. Ando, and M. Yamazaki, Jpn. Pat. 60/137,951,A2, (1985) (to Hitachi Cable, Ltd.); *Chem. Abstr.*, **104**, 6662e (1985).
33. Jpn. Pat. 58/213,022,A2 (1983) (to Sumitomo Bakelite Co. Ltd.); *Chem. Abstr.*, **101**, 181201P (1983).
34. H. Saito, H. Kitano, and F. Tanimoto, Jpn. Pat. 50/30,079 (1975) (to Nippon Kasei Co., Ltd.); *Chem. Abstr.*, **84**, 164856u (1975).
35. K. A. Kornev, K. K. Khomenkova, L. G. Balitskaya, O. K. Koshevoi, E. M. Nabutovskaya, and L. A. Shcherbina, *Plast. Massy*, **1**, 22 (1971).
36. Z. S. Egorova, V. I. Dakin, and V. L. Karpova, *Vysokomol. Soedin. A*, **21**, 2117-2125 (1979).
37. V. K. Dakin, Z. S. Egorova, and V. L. Karpov, *Plast. Massy*, **6**, 40-42 (1979).

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