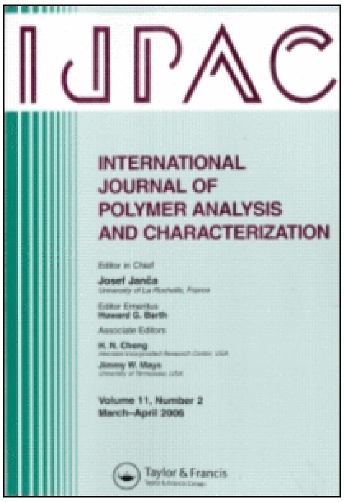

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Migration and Emission of Plasticizer and Its Degradation Products during Thermal Aging of Nitrile Rubber

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The behavior of nitrile rubber during long-term thermal aging was evaluated by following the migration of low-molecular-weight additives and additive degradation products from the material. Headspace-GC-MS analysis showed that at 60°C the number of low-molecular-weight compounds released was rather low, but a significant increase in the number and amount of products was observed when the temperature was raised from 60° to 80°C, e.g., several degradation products of tris(2-butoxyethyl)phosphate plasticizer including 2-butoxyethanol and 1-butanol were identified. Oxidation of the plasticizer was also seen in the FTIR spectra. The color of the material changed from light brown to almost black during the aging.

Keywords: Nitrile rubber; Thermal aging; Polymer degradation; Plasticizer decomposition

INTRODUCTION

Commercial plastics and rubbers are complex materials. In addition to the polymer itself, commercial formulations always contain a number of compounding ingredients (additives) that are included to give

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Address correspondence to Minna Hakkarainen, Department of Polymer Technology, Royal Institute of Technology (KTH), S-100 44 Stockholm, Sweden. E-mail: minna@polymer.kth.se particular physical and/or chemical properties. These additives include plasticizers, extender oils, carbon black, inorganic fillers, antioxidants, antiozonants, antifatigue agents, heat and light stabilizers, tackifying resins, processing aids, cross-linking agents, accelerators, retarders, adhesives, pigments, smoke and flame retardants, and others. Because of the environmental concern for chemical pollution, the total composition of the polymeric materials has become an important issue. The manufacturing worker, the polymer processing and fabricating worker, and, finally, the consumer, should not be exposed to toxic substances, e.g., additives, residual volatiles, or degradation products that migrate from the polymeric materials. Besides environmental issues, the migration of additives also changes the properties and shortens the service life of polymeric products.

Nitrile rubber (NBR), the copolymer of butadiene and acrylonitrile, is an important material in many applications due to its good oil resistance and low gas permeability. It is often used in gaskets and seals. Nitrile rubber is, however, relatively sensitive to aging due to the unsaturated backbone of the butadiene part. Several authors have investigated the thermal degradation and degradation products of nitrile rubber[1–3] at relatively high temperatures (150°–800°C). Ammonia, hydrogen cyanide, and short-chain hydrocarbons were formed during thermal degradation of nitrile rubber at 350°–400°C[3]. Series of aliphatic nitriles were detected after thermal decomposition of polyacrylonitrile at temperatures of 400°, 600°, and 800°C[4]. HCN was the predominant toxic product and its quantity increased at higher temperatures. Pyrolysis products from poly(acrylonitrile-butadiene-styrene) included phenyl-substituted aliphatic nitriles and dinitriles[5].

Only in a few cases were lower temperatures (85°–110°C) and longer aging times (0–25 days) applied to the study of the long-term properties of the material under accelerated aging conditions[2,6–8]. The effects of aging were evaluated by following the changes in tensile properties or oxidation profiles as measured by Fourier transform infrared (FTIR) or chemiluminiscence. We have shown in earlier studies that the degree of oxidation in the polymer matrix and the mechanical properties correlate with the release of low-molecular-weight compounds[9–12]. In the present study the long-term properties of nitrile rubber were evaluated by subjecting it to long-term aging for periods up to 248 days at moderate temperatures (60° and 80°C). The main focus was the analysis of low-molecular-weight compounds migrating from the material during aging. This migration of plasticizer from the material has a large influence on material properties and shortens the service life of the product.

EXPERIMENTAL

Material and Degradation Procedure

Commercial-grade compounded NBR, without carbon black, was supplied by SKEGA AB, Ersmark, Sweden. The NBR used was a mixture of two NBR rubbers with acrylonitrile content of 18% and 33%, resulting in an average of 28% acrylonitrile. Tris(2-butoxyethyl) phosphate, KP-140, was used as a plasticizer. The curing time and temperature were 5 min at 174°C. More detailed description of the material is given in Table I. To study the long-term behavior, nitrile rubber was thermally oven aged at 60° or 80°C. The rubber was cut into small pieces and 100 mg of it was weighed and sealed into each headspace vial. The aging times varied from 0 to 248 days. To follow the migration of the volatile compounds from the materials, air from the vials was analyzed by headspace–gas chromatography–mass spectrometry (headspace-GC-MS). To follow the changes on the surface composition of the material the samples were also analyzed by FTIR.

Headspace-Gas Chromatography-Mass Spectrometry

After different oven-aging times, the vials were thermostated for 50 min at 100°C in a Perkin-Elmer 101 headspace device. The air from the vial was then injected into a Perkin-Elmer 8500 model GC coupled to an ion trap detecter (ITD) mass spectrometer to separate and identify

TABLE I Description of the material and the additives used

Compound	Trade name and source
NBR	Nipol DN 212, Nippin Zeon, and Perbunan NT 1845, Bayer
ZnO	ZnO, aktiv, Bayer
Stearic acid	
Alkylated diphenylamine	Octamine, Uniroyal
Trimethyl dihydroquinone	Flektol, Monsanto
Sulfur	Struktol SU105, Schill & Seilacher
Tris(2-butoxyethyl) phosphate	KP-140
Dimethyldiphenylthiurame disulfide	Vulkacit I, Bayer
Tetramethylthiuram disulfide	TMTD

volatile products. The column used was a DB-225 (50%-cyanopropylphenyl)-methylpolysiloxane, 30 × 0.32 mm) from J&W scientific (Folsom, CA). The column temperature was held 8 min at 40°C and then programmed to 200°C at 5°C/min.

Fourier Transform Infrared Spectroscopy

FTIR analysis was performed on a Perkin-Elmer 1760 FTIR spectrometer with a 4 × beam condenser. To use the attenuated total reflection technique (ATR), the instrument was equipped with a micro ATR holder and a KRS-5 prism with incident angle of 45°.

RESULTS AND DISCUSSION

The chromatograms in Figures 1 and 2 show the large number of volatile compounds that are formed and able to migrate from the material even at the relatively low aging temperatures of 60° and 80°C. The numbered peaks are identified in Table II. A large increase in the number and amount of products was seen when the temperature was raised from 60° to 80°C. Trace amounts of 2-butoxyethanol and *N*-methylaniline were seen in the headspace-GC-MS chromatograms even before the aging. Figure 1 shows that at 60°C only a few new products, e.g., *N*,*N*-dimethylformamide and 1-butanol, were formed during 248 days. The main products in the chromatograms after aging were 2-butoxyethanol and *N*-methylaniline. The concentration of 2-butoxyethanol increased to several times the original concentration and the concentration of *N*-methylaniline first increased, but started decreasing after 180 days.

Seen in Figure 2 is a large number of low-molecular-weight compounds that migrated from the material during aging at 80°C. *N*,*N*-dimethylformamide and 1-butanol that were formed in low concentrations at 60°C appeared after only, 16 days at 80°C, and their amount increased rapidly on prolonged aging. The area of the 2-butoxyethanol peak increased to 100 times the original peak area after 7 days. After 248 days the size of the 2-butoxyethanol peak was several thousand times the original peak area in the unaged sample. Around 25 times more 2-butoxyethanol was formed during 248 days at 80°C as compared to the same time period at 60°C. Concentration of *N*-methylaniline decreased after an initial rapid increase. It was the only product that was formed in larger concentration at 60°C than at 80°. This can be related to the low thermal stability of *N*-methylaniline. After 248 days at 80°C, around 20 peaks were present in the chromatograms. The large increase of 2-butoxyethanol is logical because of the large amount of the phosphate additive in the original material. Several easily oxidizable ether bonds in

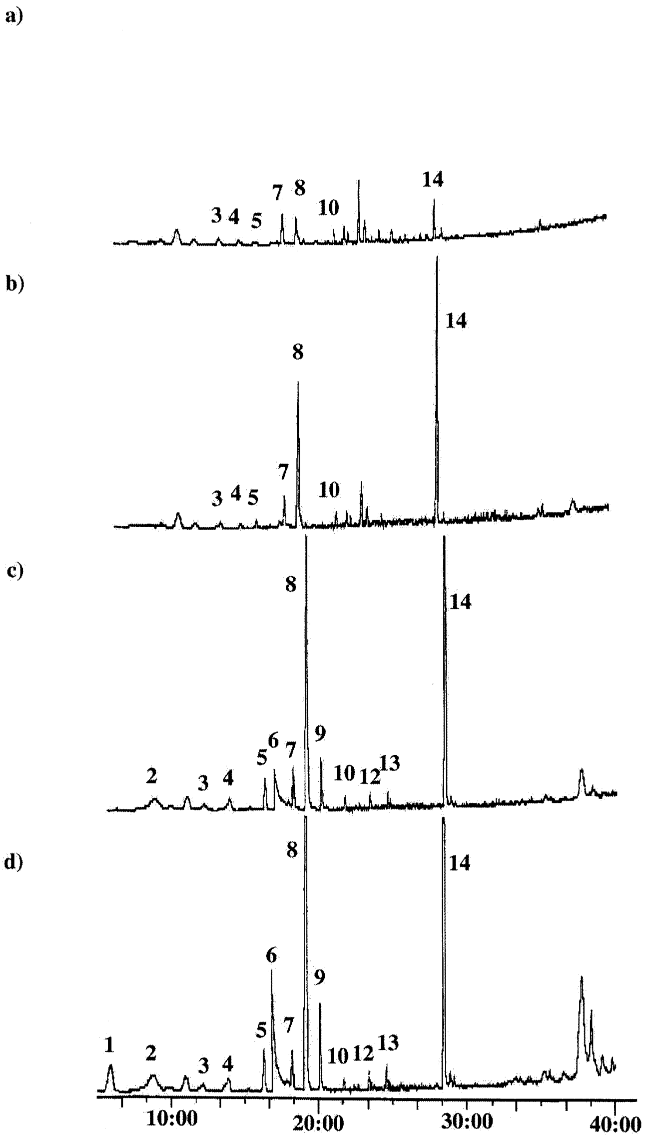


FIGURE 1 Headspace-GC-MS chromatograms of the volatile compounds that had migrated from nitrile rubber after (a) 0 days, (b) 14 days, (c) 140 days, and (d) 248 days at 60°C. The numbered peaks are identified in Table II.

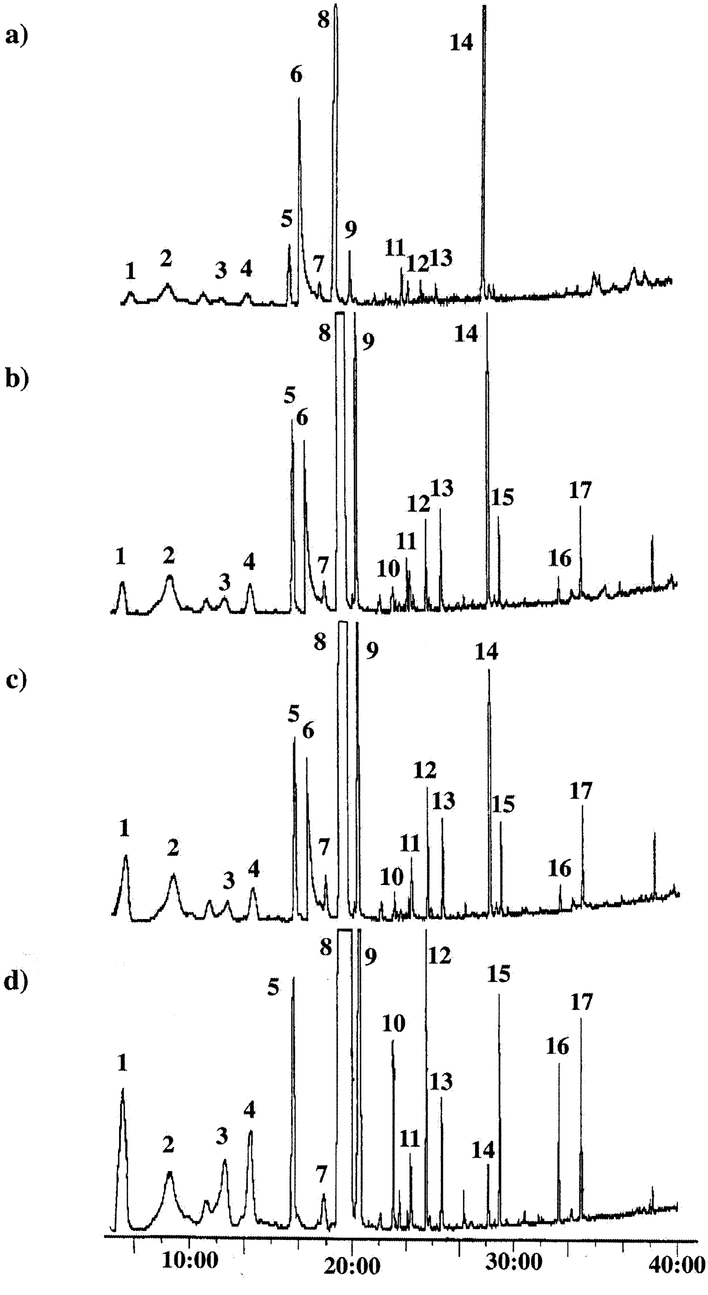


FIGURE 2 Headspace-GC-MS chromatograms of the volatile compounds that had migrated from nitrile rubber after (a) 14 days, (b) 84 days, (c) 140 days, and (d) 248 days at 80°C. The numbered peaks are identified in Table II.

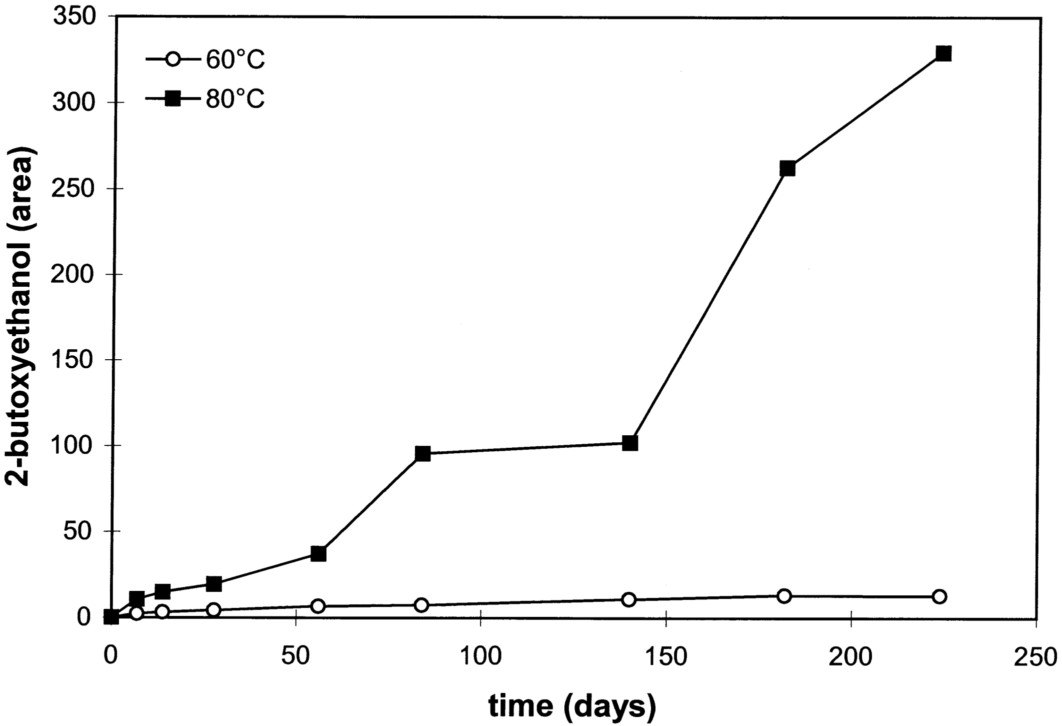
the phosphate plasticizer make it easily degradable even at the low temperatures used, and most of the products seen in the chromatograms were different hydrolysis or oxidation products from the plasticizer. Other products that were formed during aging at 80°C were dimethylurea and tetramethylurea. It has been shown earlier that tetramethylurea is formed when tetramethylthiuram disulfide (TMTD) and zinc oxide (ZnO), both present in the studied nitrile rubber material, were allowed to react at 140°C[13]. Figure 3 shows the relative area of 1-butanol, 2-butoxyethanol, *N*,*N*-dimethylformamide, and *N*-methylaniline as a function of degradation time at 60°C and at 80°C.

Parallel with the migration of low-molecular-weight compounds, oxidation of nitrile rubber matrix took place, resulting in discoloration of the samples. In accordance with headspace-GC-MS results, this discoloration was more severe at 80°C as compared to 60°C. At 80°C the material turned from yellowish to medium brown during the first 30–60 days. After 100 days the material was dark brown or almost black. Figures 4 and 5 show FTIR spectra after different aging times at 60° and 80°C. The characteristic band at 2240 cm^{-1} is attributed to the nitrile group in acrylonitrile, while the strong bands at 1275, 1130, 1040, and 970 cm^{-1} originate from the phosphate plasticizer. The intensity of $-$CN stretching

TABLE II Low-molecular-weight compounds identified after thermo-oxidation at 60°C or 80°C

Peak	Compound
1	1-Butanol[a]
2	Hydrocarbon
3	Hydrocarbon
4	Hydrocarbon
5	[a]
6	[a]
7	Butanoic acid butyl ester[a]
8	2-Butoxyethanol[a]
9	*N*,*N*-dimethylformamide
10	[a]
11	Dimethylurea
12	[a]
13	Tetramethylurea
14	*N*-methylaniline
15	[a]
16	[a]
17	[a]

[a] Degradation product of tris(2-butoxyethyl) phosphate.



(a)

FIGURE 3 Relative amounts of (a) 2-butoxyethanol, (b) 1-butanol, (c) *N*,*N*′-dimethylformamide, and (d) *N*-methylaniline as a function of aging time.

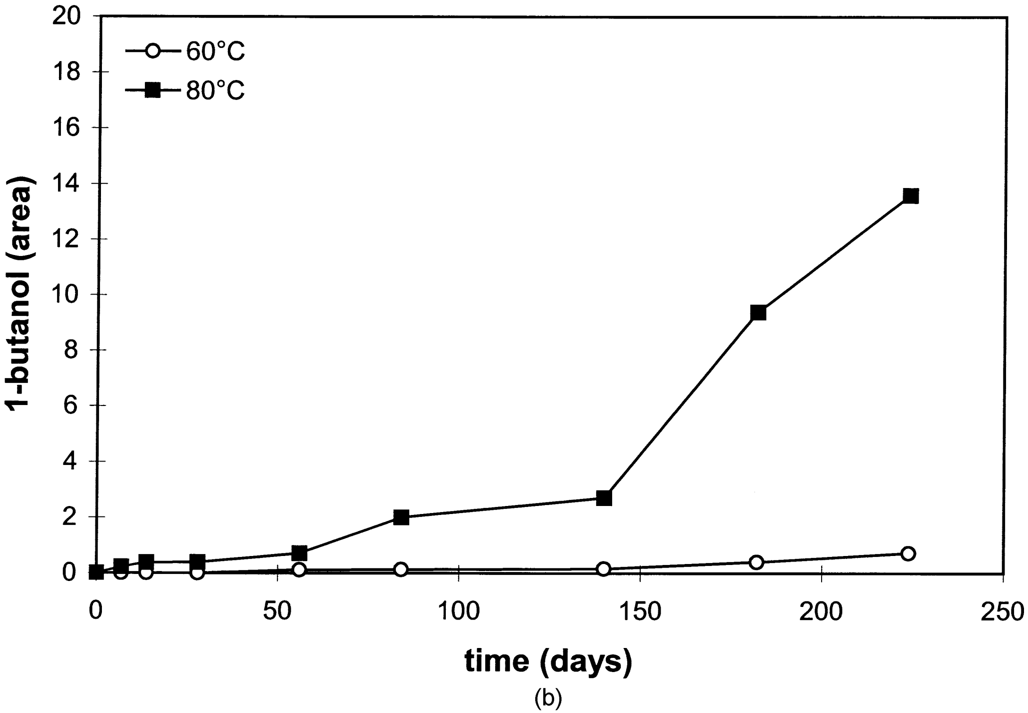


FIGURE 3 Continued.

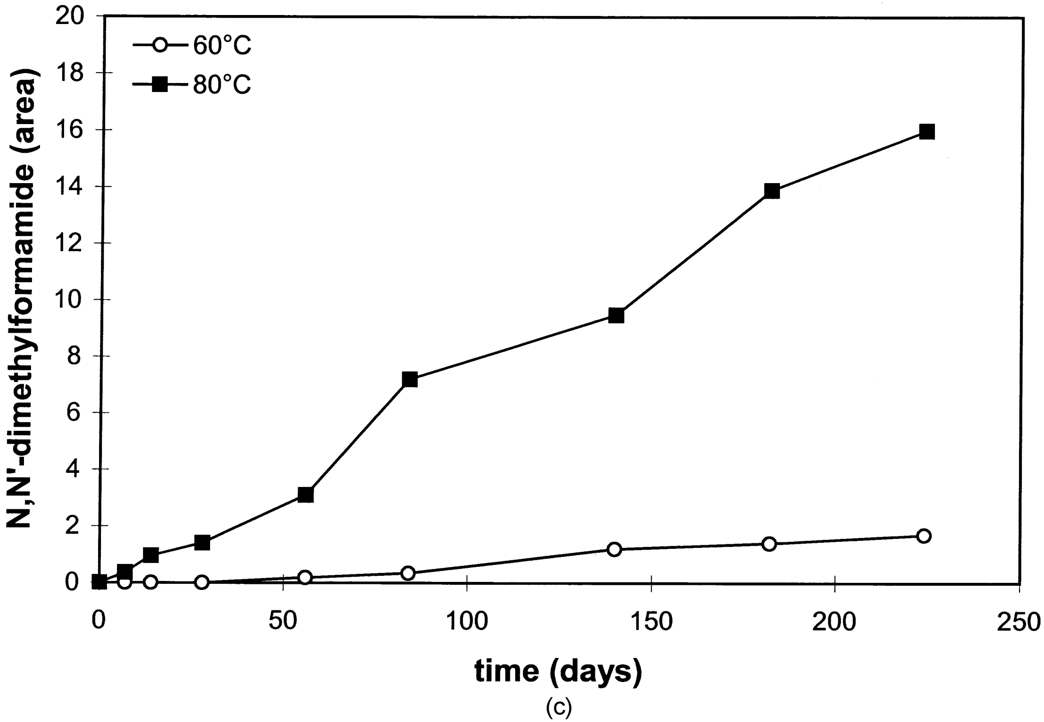


FIGURE 3 Continued.

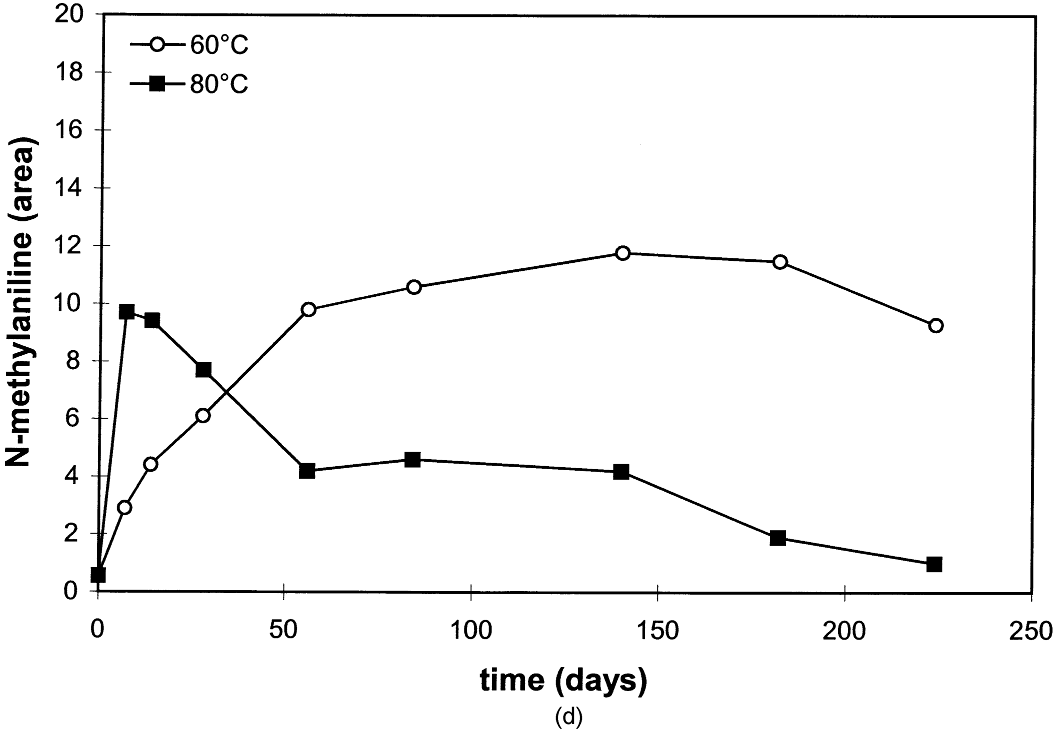


FIGURE 3 Continued.

at 2240 cm^{-1} decreased drastically during the long-term aging both at 60° and 80°C, and after 248 days the nitrile band had almost totally disappeared. The decrease in the nitrile absorbance and the formation of cyclic structures during thermo-oxidation of polyacrylonitrile is a well-known phenomenon and has been reported to happen even at relatively low temperatures, such as 150°C[14,15]. The nitrile group in nitrile rubber has, however, been reported to be insensitive to aging at temperatures below 150°C[1,2]. During photo-oxidation of nitrile rubber, the radicals generated on the nitrile group abstracted hydrogen from adjacent butadiene units, resulting in cross-linking and cyclization[16]. The decrease in nitrile absorbance observed in our study may be explained by the considerably longer aging times used. The large amount of easily oxidizable phosphate plasticizer in the material also accelerates the degradation of the polymer matrix by increasing the amount of hydroperoxides and the oxygen permeability of the material. This was shown in an earlier study

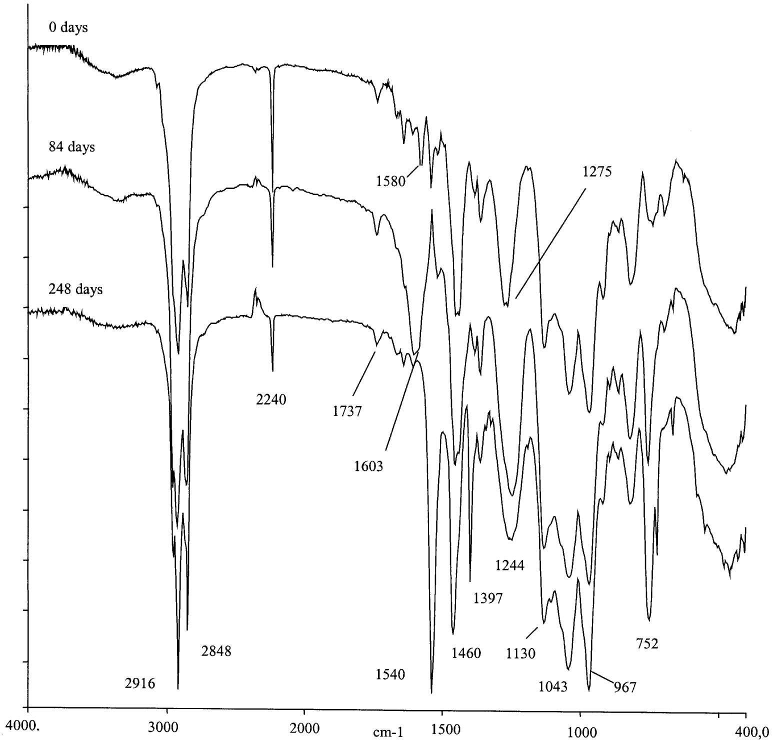


FIGURE 4 FTIR spectra showing changes in surface composition after 0 days, 84 days, and 248 days at 60°C.

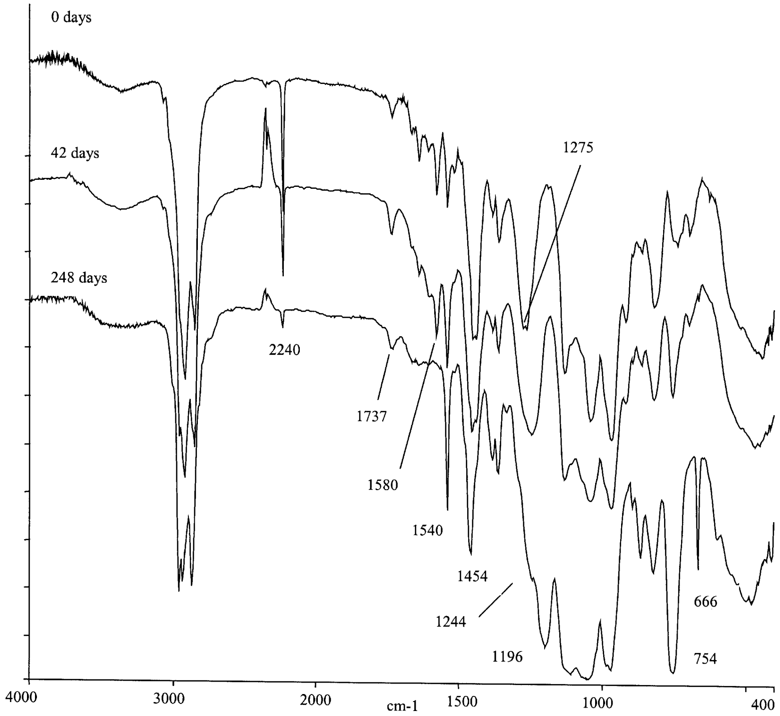


FIGURE 5 FTIR spectra showing changes in surface composition after 0 days, 42 days, and 248 days at 80°C.

where the chemiluminiscence (CL) signal during thermo-oxidation was much higher for NBR plasticized with tris(2-butoxyethyl)phosphate than for NBR without plasticizer, indicating a higher degree of hydroperoxides in the plasticized NBR material[8]. The α position of ethers is easily attacked by oxygen, and the CL signal from pure plasticizer was very high due to a large number of hydroperoxides. In another study, the activation energy of unfilled rubber was considerably larger compared to the activation energy of carbon black–filled material, and the filled material showed a much faster degradation[2].

Along with the decrease in nitrile absorbance, other changes were observed in the FTIR spectra. These changes were mostly associated with the different additives in the nitrile rubber. The band originally located at 1275 cm^{-1} associated with the phosphoric ester group shifted to 1244 cm^{-1} after 21 days at 80°C. After 248 days at 80°C the band had shifted further to 1196 cm^{-1}, with a small shoulder remaining at 1244 cm^{-1}. At 60°C a shift to 1244 cm^{-1} was observed after 84 days. This shift shows that the phosphate plasticizer was oxidized, and in accordance with headspace-GC-MS results this oxidation was faster and more severe during aging at 80°C. The original weak band at $1580\,\mathrm{cm}^{-1}$ attributed to zinc carboxylates[17–19] broadened and increased in intensity at the beginning of the thermo-oxidation. However, on prolonged aging it again decreased and had totally disappeared after 56 days at 80°C and after 84 days at 60°C. Other changes in the FTIR spectra were the formation of new rather strong bands at $1540\,\mathrm{cm}^{-1}$ and $1397\,\mathrm{cm}^{-1}$ and an increase in the absorbance at $750\ \mathrm{cm}^{-1}$.

In earlier studies, a broad band at $3490\,\mathrm{cm}^{-1}$ in the hydroxyl vibration region of the IR spectra was formed during low-temperature thermo-oxidation of nitrile rubber[20]. In the carbonyl stretching region, the band at $1692\,\mathrm{cm}^{-1}$ continuously increased, and a broad band with maximum at $1725\,\mathrm{cm}^{-1}$ appeared and steadily increased. An increase in the $-\mathrm{C{=}O}$ and $-\mathrm{COOR}$ functionalities at 1760–$1720\,\mathrm{cm}^{-1}$ and 1230–$1000\,\mathrm{cm}^{-1}$was observed after degradation at 75°–150°C in air and nitrogen[21]. We could not, however, detect any significant changes in hydroxyl or carbonyl regions, and possible changes in the 1230–$1000\,\mathrm{cm}^{-1}$ region were shadowed by the strong absorbance from the phosphate plasticizer.

CONCLUSIONS

At 60°C the formation and emission of low-molecular-weight compounds from nitrile rubber was low; however, a large increase in the number and amount of products was observed when the temperature was raised from 60° to 80°C. Loss of plasticizer, tris(2-butoxyethyl)phosphate and its degradation products, was observed during aging at both 60° and 80°C. A small amount of 2-butoxyethanol was already present in the unaged samples, and it was the main low-molecular-weight product migrating from the material during aging. Around 25 times more 2-butoxyethanol was released from the material during 248 days at 80°C as compared to the same time period at 60°C. In addition to the degradation products from the phosphate additive, *N,N*-dimethyl formamide, dimethylurea, tetramethylurea, *N*-methylaniline, and short-chain hydrocarbons were identified. FTIR analysis showed that the intensity of the characteristic $-\mathrm{CN}$ stretching at $2240\,\mathrm{cm}^{-1}$ decreased during aging, and after 248 days the nitrile band had almost totally disappeared. The band, originally located at $1275\,\mathrm{cm}^{-1}$, attributed to the phosphate plasticizer, was shifted to $1244\,\mathrm{cm}^{-1}$ and to $1196\,\mathrm{cm}^{-1}$ during 248 days at 60° and 80°C, respectively, showing oxidation-induced changes in the chemical structure of the phosphate plasticizer. The color of the material gradually changed from light brown to almost black during the thermal treatment. This color change was more significant during aging at 80°C than at 60°C.

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