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A PRELIMINARY STUDY OF SOME METHODS FOR FOLLOWING THE ACCELERATED AGING AND LIFE PREDICTION OF RUBBERS

J. A. Hiltz - S.C. Hattie

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A PRELIMINARY STUDY OF SOME METHODS FOR FOLLOWING THE ACCELERATED AGING AND LIFE PREDICTION OF RUBBERS

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March 1989

Approved by L.J. Leggat
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Abstract

Forty three rubber samples aged at temperatures between 70°C and 150°C for periods up to three hundred days were investigated using hardness tests, dynamic mechanical analysis and pyrolysis-gas chromatography-mass spectrometry to determine if these techniques might be useful in monitoring the aging of the samples. The samples were formulated and aged at ARE Holton Heath and included twenty seven acrylonitrile-butadiene rubber samples, twelve polychloroprene rubber samples, and four polyisoprene rubber samples. All three techniques were capable of monitoring changes in the rubbers which correlated with the time and temperature of exposure of the samples. However, successful application of these techniques to the quantitative prediction of lifetime of elastomers from accelerated tests will require further experimentation. CANADA. JES)

Résumé

On a examiné 43 échantillons de caoutchouc vieillis à des températures comprises entre 70 et 150°C pendant des périodes pouvant atteindre 300 jours, en effectuant des essais de dureté, des essais mécaniques en conditions dynamiques et des essais de pyrolyse avec analyse par chromatographie gazeuse et spectrométrie de masse, afin de déterminer si ces techniques peuvent servir à établir l'âge des échantillons. Les échantillons ont été formulés et vieillis à la ARE Holton Heath et comprenaient 27 échantillons d'acrylonitrile-butadiène, 12 échantillons de polychloroprène et 4 echantillons de polyisoprène. Les trois techniques permettaient de mesurer dans les caoutchoucs des changements qui étaient en corrélation avec la durée et la température d'exposition des échantillons. Toutefois, il faudra effectuer d'autres études avant d'utiliser ces techniques pour prévoir quantitativement la durée utile des élastomères à partir de résultats d'essais accélérés.

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1.0 Introduction

Polymeric materials degrade by a number of mechanisms including thermal, oxidative, radiative, chemical, biological and mechanical routes[1]. Degradation or aging of a polymeric material is often accompanied by one or more of the following physical changes; hardening, embrittlement, softening, cracking, crazing and discoloration. These physical changes correlate with changes in the structure and composition of a polymeric material such as molecular weight distribution, degree of cross-linking, crystallinity, and loss of additives[2,3]. For instance, thermal degradation can lead to an increase in the cross-link density and a concomitant increase in molecular weight or it can cause bonds to be broken and result in a decrease in molecular weight or it can result in the volatilization of additives such as plasticizers. Radiative degradation can result in the breaking of bonds[4], while chemical degradation can result in plasticization or dissolution of the polymer[5]. Mechanical degradation of a polymer generally results in the breaking of bonds[6].

In all instances, these changes have an effect on the chemical and mechanical properties of the material. The knowledge of how these changes affect the ability of a material to do the job it was designed to do is important in predicting the remaining life of the material.

Thermal degradation of polymeric materials can involve four mechanisms; depolymerization, random chain scission, cleavage of side groups which is followed by cyclization or fragmentation and/or inter-chain condensation or cross-linking[7]. Further, many polymers contain additives such as plasticizers which may volatilize over a period of time.

A number of methods have been used to monitor the thermal degradation of polymeric materials. These include thermogravimetric analysis[8-12] (TGA) which measures weight loss with temperature change, differential thermal analysis[13,14] (DTA) which monitors the difference in the temperature of an inert standard and a sample against the temperature of the sample as both sample and reference are heated, differential scanning calorimetry[15] (DSC) which measures the heat flow to or from a sample as a function of temperature, thermal volatilization analysis[15,16] (TVA) which monitors the evolution of volatiles by sensing pressure changes as a function of temperature, and dynamic mechanical analysis[17] (DMA) which measures changes in the response of the material to an applied stress.

To utilize the results of any measurement in predicting the lifetime of a material from accelerated aging studies, the rate of change of the parameter being measured as a function of temperature must be established. If the rate and temperature data can be described by an Arrhenius relationship, Equation (1), where k is the rate (change of measured parameter with time), A is a preexponential factor, E is the activation energy for the process, R is the gas constant and T is temperature, then the rate of degradation at lower temperatures can be calculated. This allows one to predict the service life of a material at a particular temperature. If a plot of log k versus 1/T (see Equation 2) is linear then the activation energy can be calculated from the slope of the line and log A is given by the y-intercept.

$$k = A\,e^{-E/RT} \qquad (1)$$

$$\log k = -E/(2.303RT) + \log A \qquad (2)$$

The temperature dependence of the rate process is then known and the rate at the actual service temperature can be calculated.

For many practical purposes it would be useful to be able to predict the lifetime of polymeric materials used on naval vessels. Elastomers, in particular, are used in applications where the loss of desired properties with aging can affect ships operations. For instance, both anechioc tiles and engine mounts are made of elastomeric materials whose performance can deteriorate with aging.

In this paper the results of hardness, dynamic mechanical analysis and pyrolysis-gas chromatography/mass spectrometry (pyr-GC/MS) studies of samples of three rubber formulations that had been aged at elevated temperatures for periods of time up to 300 days will be reported. The study was undertaken to determine if these methods might be useful techniques to assess thermal aging of rubber samples and subsequently allow life prediction of rubber samples from accelerated testing studies. This work is contributing to a TTCP-TP3 operating assignment on the aging and life prediction of rubbers. The project has two aims; the comparison of the effects of accelerated aging with real time aging of rubber samples and the investigation of techniques that will allow measurement of the aging of a sample and facilitate quantitative service life predictions.

2.0 Experimental Approach

2.1 Materials. All rubber samples used in this study were prepared and aged at ARE Holton-Heath.The materials studied included a polyisoprene (natural) rubber - ARE Mix 1991, a polychloroprene rubber - ARE Mix 2754, and an acrylonitrile-butadiene rubber - ARE Mix 2679. The formulations of these rubbers are shown in Table 1.

TABLE 1

Formulations of the three rubbers studied in this work.

Acrylonitrile-Butadiene Rubber - Mix 2679		
Paracril 1880	-	50phr
Breon 36-70	-	50
Zinc Oxide	-	5
Stearic Acid	-	1
Nonox B	-	2
Sulfur	-	0.5
MBTS	-	1
MS	-	0.5
Philblack SR	-	60
DOS	-	6
Dutrex RT	-	4

Polychloroprene Rubber - Mix 2754		
Neoprene	-	100phr
Philblack SR	-	60
Stearic Acid	-	1
Zinc Oxide	-	5
Octamine	-	2
TMTD	-	1
Maglite D	-	4
Circosol 410	-	10

Polyisoprene (Natural) Rubber - Mix 1991		
SMR 5	-	100phr
Stearic Acid	-	1
Zinc Oxide	-	5
Santocure	-	0.8
Sulfur	-	2.5
Flectol H	-	1
Sevacarb MT	-	20

phr - parts per hundred resin

A total of 43 rubber samples were studied; 27 acrylonitrile-butadiene rubber samples, 12 polychloroprene rubber samples, and 4 polyisoprene (natural) rubber samples. The oven aging conditions for the rubber samples are listed in Table 2. For example, sample number 24A was aged for 40 days at 70°C.

TABLE 2

Aging conditions and Shore Durometer 'A' Hardnesses of test specimens.

Sample #	**Condition(time/^{o}C)**	**Hardness(Shore A)**
Acrylonitrile-Butadiene - ARE Mix 2679		
2679	not aged	65
24A	40d/70	66
25A	80d/70	67
26A	161d/70	69
27A	241d/70	71
28A	276d/70	70
18A	20d/85	66
19A	40d/85	67
20A	80d/85	71
21A	121d/85	84
22A	161d/85	79
12A	5d/100	66
13A	10d/100	68
14A	20d/100	70
15A	30d/100	75
16A	40d/100	86
17A	300d/100	99
6A	2d/125	67
7A	4d/125	71
8A	7d/125	77
10A	10d/125	80
9A	12d/125	83
11A	272d/125	97
2A	16h/150	65
3A	24h/150	67
4A	48h/150	78
5A	64h/150	81
Polychloroprene Rubber ARE Mix 2754		
100F	not aged	71
2754	control	70
71F	40d/70	75
72F	80d/70	78
82F	40d/85	78
83F	80d/85	82
93F	20d/100	81
94F	30d/100	86
95F	40d/100	87
96F	83d/100	95
103F	8d/125	86
104F	10d/125	89
Polyisoprene (Natural) Rubber ARE Mix 1991		
80N	not aged	51
96N	13d/100	50
81N	24h/150	62
95N	5d/150	53

2.2 Equipment and Experimental Conditions

2.2.1 Hardness Tests. All hardness measurements were made with a Shore Durometer 'A' hardness tester, Shore Instrument and Manufacturing Company, Jamaica, N.Y. Five hardness measurements were made on each sample and the reported hardness is the mean value of the five measurements.

2.2.2 Dynamic Mechanical Analyser (DMA). The DMA can measure dynamic properties of materials in both the fixed frequency and resonance modes. In the fixed frequency mode, an applied stress forces the sample to undergo a sinusoidal oscillation at a frequency and amplitude (strain) selected by the operator. Energy dissipated by the sample causes the strain to be out of phase with the applied stress. In this instance the stress can be factored into two components, one in phase with the strain and the other that leads the strain by 90 degrees. The phase angle between the applied stress and and resulting strain is measured by the instrument and used along with the maximum stress and strain amplitudes to calculate the storage modulus, the ratio of the in-phase stress to the maximum strain amplitude and the loss modulus, the ratio of out-of-phase stress to the maximum strain amplitude of the sample along with other viscoelastic properties. The fixed frequency mode can be used at frequencies between 0.001 Hz and 10 Hz and is used primarily for low modulus samples such as rubbers.

Dynamic mechanical analyses were carried out in the fixed frequency mode at 1 Hz using a temperature ramp of $5^{o}C$/min from $-120^{o}C$ to $50^{o}C$ on a Dupont model 983 Dynamic Mechanical Analyser (DMA). A Dupont microprocessor controlled liquid nitrogen cooling assessory was used for work at subambient temperatures.

The analysis was conducted on the following samples, polychloroprene rubber samples numbered 2754, 93F, 95F, and 96F which had been aged for 0, 20, 40, and 83 days respectively at $100^{o}C$ and acrylonitrile-butadiene rubber samples numbered 2679, 13A, 14A, 15A, 16A, and 17A which had been aged for 0, 10, 20, 30, 40, and 300 days respectively at $100^{c}C$, to determine if this technique could give insight into the aging process for these rubbers.

2.2.3 Pyrolysis-Gas Chromatography/Mass Spectrometry (pyr-GC/MS). Pyrolyses were conducted on a Chemical Data Systems Model 170 Pyroprobe which was connected to a Finnigan MAT 5100 gas chromatograph/mass spectrometer (GC/MS) using a standard interface heated at 300°C. Conditions for the pyrolyses are shown in Table 3. Samples, typically between 0.4

mg and 0.7 mg, were pyrolyzed at either 300°C or 995°C in an inert atmosphere (helium) for ten seconds in 20 mm quartz tubes using a platinum coil probe. The pyrobrobe heating rate was set at the ramp "off" position (660°C/sec).

TABLE 3

Conditions used for the flash pyrolysis (coil pyroprobe) of the rubber samples using a CDS Model 770 Pyroprobe.

Pyrolysis Temperature	300°C, 995°C
Pyrolysis Time	10 seconds
Ramp	off
Heating Rate	660°C/sec
Sample size	0.4-0.7 mg
Interface Temperature	300°C

The separations and identifications of degradation products were made on a Finnigan MAT 5100 capillary GC/MS with a SuperIncos™ data system. A Finnigan 9611 capillary GC with a DB-1 100% methyl silicone column (30m long X 0.25mm inside diameter) was used for all separations. Helium at a flow of approximately 1.0 mL/min (40°C) was used as the carrier gas for all analyses. The data system was equipped with the National Bureau of Standards Library of appproximately 38,000 mass spectra.

Data were acquired for 40 minutes in the full scan mode from 25 to 475 atomic mass units (amu) for the polychloroprene rubber, and from 35 to 475 amu for the acrylonitrile-butadiene and polyisoprene (natural) rubbers using a 1.87 or 2.00 second scan. The program used to control the capillary GC oven was as follows. The oven was kept at 40°C for four minutes, then ramped at a rate of 10°C/min to 300°C where it remained for ten minutes.

3.0 Results and Discussion

The results of the hardness tests, dynamic mechanical analysis, and pyr-GC/MS analysis of the rubber samples are presented and discussed separately.

3.1 Shore Durometer 'A' Hardness. The Shore Durometer 'A' hardnesses of the rubber samples are shown in Table 2. A plot of the hardnesses of the acrylonitrile-butadiene rubber samples against the logarithm of time of exposure in days at 70°C, 85°C, 100°C, 125°C, and 150°C is shown in Figure 1. The results indicate that hardness increases with time of exposure at a particular temperature. For instance, the hardnesses of acrylonitrile-butadiene rubber samples 12A through 17A which were heated at 100°C from 5 days to 300 days were found to increase from 66 for the sample exposed for 5 days to 99 for the sample exposed for 300 days. Samples 6A through 11A were heated at 125°C from 2 days to 272 days and as was observed for the samples heated at 100°C, the hardnesses of the samples increased, in this case from 67 to 97.

The rate of change of hardness was also found to be temperature dependent, that is, the change in hardness for a particular exposure time increased as the temperature increased. Comparison of the hardnesses of the samples exposed at 100°C and 125°C indicates that hardness increases more rapidly for the samples exposed at the higher temperature, i.e., the hardness increased from 65 to 83 in 12 days for the samples exposed at 125°C, while it took approximately 40 days for the same change in hardness to be observed for the samples heated at 100°C. Another example of this is found for samples 24A, 19A, and 16A. The samples were all exposed for 40 days but the exposure temperature was 70°C for 24A, 85°C for 19A and 100°C for 16A. The resulting hardnesses were 66, 67 and 86 respectively.

The hardness data for the acrylonitrile-butadiene samples were analysed to determine if they would fit an Arrhenius type equation, that is, an equation that would give the temperature dependence of the rate of change of hardness. The rate of change of hardness (k) at each temperature was determined by plotting of the natural logarithm of the ratio of the hardnesses of the samples at time t (H_t) and the hardness of the unaged sample (H_o) against time (t). The data was found to fit equation 3.

$$\ln H_t/H_o = kt \qquad (3)$$

The rates of change in hardness (k) at each temperature were obtained from the slopes of these plots. Log k values were then plotted against the reciprocal of the temperature and from the slope and y-intercept of the resulting straight line ($r^2 = 0.99$) the 'activation energy' (E_a) and preexponential factor (A) were determined (see equation 2 in the Introduction). The plot is shown in Figure 2. Since the preexponential factor and the 'activation energy' for the change in hardness of these samples had been determined, equation 1 could be used to determine the rate of change of hardness at any temperature, and in conjunction with equation 3 this could be used to predict the time for the sample to undergo a particular change in hardness. It should be noted that only thermal aging of the sample has been considered in this treatment and that other degradation mechanisms will also affect the rate of change of any measurable property of these rubbers.

The increase in the hardness of these rubber samples may have been caused by an increase in cross-link density and/or the loss of additives such as plasticizers. It is also possible that as thermal aging increased, bonds in the rubber broke and led to a decrease in the hardness of the rubbers samples. This was not apparent from the results for the acrylonitrile-butadiene rubbers although this might have been masked by the concomitant loss of additives such as plasticizers which tends to increase hardness.

Similar trends, that is, increases in hardness with exposure time at a particular temperature and increases in the rate of change of hardness with temperature, were observed for the polychloroprene rubber samples. Exposure of a sample at 85°C for 40 days (sample 82F) resulted in a greater change in hardness than an 80 day exposure at 70°C (sample 72F). The hardness was also found to increase as the time of exposure at a particular temperature was increased. For example, the hardness of samples 93F through 96F increased from 81 to 95 as the time of exposure was increased from 20 days to 83 days.

Relationships involving aging temperature, time of exposure and change in hardness were less evident with the polyisoprene samples. This is probably influenced by the small number of samples received for analysis and a larger data base is probably required for a better analysis. The results for samples 81N and 95N, exposed at 150°C for 1 day and 5 days respectively suggest that the effect of thermal aging is first to increase cross-link density and volatilize additives such as plasticizers which results in an increase in hardness. As the thermal aging increases bonds start to cleave which results in reduced hardness.

3.2 Dynamic Mechanical Analysis. Rubbers exhibit a viscoelastic response to an applied stress. That is, their response to an applied stress or strain is intermediate between that of ideal elastic materials, where the material deforms immediately to a strain in response to a stress and ideal Newtonian fluids which support no stress and immediately exhibit viscous flow in response to a shearing stress. Creep and stress relaxation are examples of the viscoelastic response of polymeric materials to a constant load and stress respectively. In both the response of the material to a stress or strain is found to be time dependent. Dynamic techniques involve the use of a periodically varying stress or strain on the sample and as is found for the static tests, i.e., creep and stress relaxation, the properties measured are found to be time dependent.

The response of a polymer to a periodically varying stress or strain is dependent on a number of factors including the magnitude of the applied stress or strain, temperature, the time frame of the experiment, structure (e.g., degree of cross-linking), and presence of additives[3,17-20]. If variables such as the magnitude of the load, temperature, and the time frame of the experiment are kept constant then differences in the dynamic response of various materials can be related to changes in the structure of a material such as degree of cross-linking, degree of crystallinity, molecular orientation or changes in the chemical composition of the material such as loss of additives.

3.2.1 DMA of Polychloroprene Rubber. Figures 3 through 6 show the plots of the variation of the storage modulus (E'), the loss modulus (E''), and Tan δ, the ratio of the loss modulus to the storage modulus for the polychloroprene samples aged at 100°C for 0, 20, 40, and 83 days respectively against temperature. Typically in the region of the glass transition temperature (T_g) there is a decrease in the storage modulus curve, a peak in the loss modulus curve, and a peak in Tan δ curve.

The glass transition temperature has been determined from dynamic mechanical data in several ways. These include the intersection of the tangents to the modulus (E') curve in the region of the maximum change in slope, the peak in the E" curve and the peak in the Tan δ curve. It is obvious from Figures 3 through 6 that the measured T_g for a particular material is dependent on the parameter used to measure it. Generally, the T_g determined from the E' curve is lower than that measured from the E" curve, which is lower than that measured from the Tan δ curve. It is important when comparing T_g values for a series of compounds that only T_g values measured using the same parameter be compared.

The measured Tan δ values for the polychloroprene samples are indicated in Figures 3 through 6 and are listed in Table 4 along with T_g determined from the E' curve.

Table 4

Variation in glass transition temperatures (T_g) and Tan δ maximum of polychloroprene rubbers aged at 100°C for times shown.

Sample #	**time at 100°C**	**T_g**	**Tan δ**
100F	unaged	-28.7	1.07
93F	20 days	-27.8	0.81
95F	40 days	-24.6	0.68
96F	83 days	-23.3	0.44

Both T_g and Tan δ were observed to vary with time of aging, T_g increasing from -28.7°C for the unaged sample to -23.3°C for the sample aged for 83 days at 100°C, while the maximum of Tan δ decreased from 1.07 for the unaged sample to 0.44 for the sample aged for 83 days at 100°C. The increase of T_g with aging of the polychloroprene samples is consistent with either an increase in cross-link density in the samples or the loss of plasticizer from the sample[3,19,20]. Increased cross-link density increases T_g by lowering the mobility of the polymeric molecules, and results in a rubber which changes from the glassy state to the leathery or rubbery state at a higher temperature. The T_g of a polymeric material has also been shown to decrease with increased concentration of plasticizer. If plasticizer is volatilized during accelerated aging studies, then the T_g of the samples would increase as the concentration of plasticizer was reduced.

The shape of the Tan δ versus temperature curve in the vicinity of the glass transition has also been found to vary with degree of cross-linking of a sample[19-21]. That is, the height of the Tan δ peak diminishes and becomes broader as the degree of cross-linking is increased. Such a variation in the Tan δ peak is observed for the polychloroprene rubber samples as the time of aging is increased and is shown in Figure 7. It is interesting to note that the value of T_g measured from the Tan δ versus temperature curves increases with aging of the samples in a manner similar to that observed for the T_g measured from the E' curve.

3.2.2. DMA of Acrylonitrile-Butadiene Rubber. Figures 8 through 13 show the plots of E', E'', and Tan δ against temperature for samples of acrylonitrile-butadiene aged at 100°C for 0, 10, 20, 30, 40, and 300 days respectively. The storage modulus (E') of these samples at a particular temperature was observed to increase as the time of aging increased from 0 days to 300 days. This is expected as the hardnesses of the samples were found to increase with time of aging.

In contrast to the polychloroprene samples where the loss modulus (E'') showed a single maximum in the temperature range studied, E'' for the acrylonitrile-butadiene samples showed a more complicated variation with temperature. The plot of E'' against temperature for the acrylonitrile-butadiene samples aged at 100°C for 0, 10, 20, 30, 40, and 300 days is shown in Figure 14. The plot of the storage modulus against temperature for the unaged sample has two distinct peaks at approximately -30°C and 0°C while only a single peak at approximately 18°C is observed for the sample aged for 300 days. The values of the two maxima in E'' for the samples aged for 10, 20, 30, and 40 days vary smoothly. That is, the first peak decreases in intensity and the maximum moves to higher temperature for the samples aged 10 and 20 days, then increases in intensity while moving to higher temperatures for the samples aged 30 and 40 days while the second maximum increases in intensity for the samples aged 10, 20, 30, and 40 days respectively. The sample aged for 300 days shows a single maximum.

The variation of Tan δ with temperature for the acrylonitrile-butadiene samples is shown in Figure 15. The overall trend observed for Tan δ is similar to that observed for the polychloroprene samples, that is, the magnitude of Tan δ decreases as the aging of the sample is increased while the maximum in Tan δ moves to higher temperature as the time of aging is increased.

The observed changes in the parameters that describe the dynamic behavior of these acrylonitrile-butadiene samples indicate that aging of these samples is accompanied by increased cross-linking in the rubber and/or loss of a plasticizer (increased modulus, Tan δ decreasing in amplitude while the maximum occurs at higher temperature). The literature[19-21] suggests that the maximum in the loss modulus versus temperature curve should move to higher temperatures as the degree of cross-linking of a polymer increases or plasticizer concentration decreases. This was observed for these samples.

These DMA results indicate that the thermal aging process can be studied using dynamic mechanical analysis. The storage and loss moduli and tan δ of the samples studied were found to vary with time of aging. Further the interpretation of the results support both the loss of additives and increased cross-link density mechanisms for the observed change in hardness for the two series of rubbers studied. In order to use DMA data to predict lifetime of rubbers from accelerated aging studies, dynamic mechanical analysis of rubbers aged at various temperatures would have to be completed.

3.3 Pyrolysis - Gas Chromatography/Mass Spectrometry (GC/MS). Pyrolysis-GC/MS is a destructive analytical technique, i.e., the material to be analysed is degraded and fragments of the material are separated, detected and identified. This technique has been used to study a wide range of polymeric materials[22-31] including paints, thermoset and thermoplastic materials, and elastomeric materials. Knowledge of the degradation products of polymeric materials has been used to study degradation mechanisms[32-34], to identify changes in composition[35,36] and to monitor the evolution of toxic and hazardous gases[37]. Pyrolysis temperatures between 300°C and 1000°C have been used, although temperatures between 600°C and 1000°C are more common. The reproducibility of the results derived from this technique has been shown to be very sensitive to the rate at which the sample is heated and the sample size and its geometry.

The very nature of rubbers, i.e., the presence of anti-oxidants, accelerators, and other additives and the dependence of properties on the degree of cure and cross-linking, makes comparison of samples after varying aging treatments a difficult problem. To use pyrolysis GC/MS to determine aging of a material requires that differences in the pyrograms can be related to changes in the material. These differences might be observed in the structure and the relative abundance of the degradation products or could involve the loss of additives such as anti-oxidants, heat and uv stabilizers, and/or plasticizers.

In the following section, the reconstructed ion chromatograms (RICs) of the three elastomers will be discussed separately. The analysis is based on comparisons of the RICs obtained after pyrolysis at 300°C and 995°C for each sample. Any changes in the chromatographic 'fingerprint', that is, the types and relative intensities of compounds detected were then related to variation in aging. Emphasis was placed on the changes observed with aging history in an attempt to determine whether pyrolysis-GC/MS provided an acceptable method of assessing the accelerated aging of elastomeric materials.

The positions of the various peaks in the RICs will be referred to by scan number rather than retention time. However retention time in minutes can be determined by multiplying scan number by the time per scan and dividing by 60.

3.3.1 Polychloroprene Rubber. Figure 16 shows the RIC of an unaged sample of polychloroprene rubber pyrolysed at 300^{O}C. The pyrogram can be separated into three areas of interest, scans 1 to 600, scans 600 to 850, and scan 994. The peaks found below scan 600 have been attributed to the thermal degradation of the polychloroprene rubber, while the peaks between scans 600 and 850 and the peak at 994 have been attributed to additives. Figures 16 through 19 show the RICs following pyrolysis at 300^{O}C of polychloroprene samples aged at 100^{O}C for 0, 30, 40, and 83 days respectively. Other than the disappearance of a major peak (scan 994, Figure 16), the 'fingerprints' for the four samples are similar.

The RICs following pyrolysis at 995^{O}C of the samples aged 0, 20, 30, and 83 days at 100^{O}C are shown in Figures 20 through 23. As was observed for the samples pyrolysed at 300^{O}C, the intensity of the peak at scan 987 (in Figure 20) was found to decrease as aging time was increased. In addition, the intensity of the group of peaks located between scans 600 and 850 was observed to decrease in intensity as the aging of the samples was increased. The other peaks in the RIC are similar for all compounds and have been determined to be characteristic of this particular polychloroprene rubber. Compounds such as 2-chloro-1,3-butadiene, toluene, and dimethylbenzene are characteristic degradation products of this material. The presence of these degradation products indicates that this polychloroprene rubber is degrading at 300°C by two mechanisms. Random chain scission yields the monomer (2-chloro-1,3-butadiene) and loss of HCl followed by cyclization leads to the formation of the aromatics such as toluene and dimethylbenzene.

These results indicate that pyr-GC/MS may be applicable to the study of the aging of polychloroprene as the decrease in intensity of the peak at retention time 32.5 minutes and the peaks between scans 600 and 850 appear to correlate well with degree of aging. The compounds that give rise to these peaks are additives and the gradual loss of these from the polymer would result in a change in the properties of the polymer such as increased hardness and modulus.

3.3.2 Acrylonitrile-Butadiene Rubber. The RIC of an unaged sample of acrylonitrile-butadiene rubber (2679) pyrolysed at 300°C is shown in Figure 24. Two major peaks were observed at scans 798 and 916 and were determined to be the dioctyl ester of hexanedioic acid (scan 798) and the dioctyl ester of decanedioic acid or dioctyl sebacate (DOS)(scan 916). At 300°C it appears that very little pyrolysis is taking place and the major compounds are common plasticizers that were volatilized and subsequently detected and identified. The RIC of the same sample pyrolysed at 995°C is shown in Figure 25. In contrast to the RIC for the sample pyrolysed at 300°C, there are a number of peaks in the pyrogram between scans 0 and 800 which result from the breaking of bonds in the acrylonitrile-butadiene rubber in addition to the peaks due to the dioctyl esters.

The RICs following pyrolysis at 300°C of acrylonitrile-butadiene samples 12A, 13A, 14A, 15A, 16A, and 17A aged at 100°C for 5, 10, 20, 30, 40, and 300 days respectively are shown in Figures 26 through 31. Comparison of the relative intensities of the ester peaks as the aging of the sample increases indicates that the intensity of the hexanedioic acid ester peak decreases relative to that for the decanedioic acid ester peak in a manner that corresponds well with time of exposure at 100°C. For instance, the intensity of the hexanedioic acid ester peak is greater than decanedioic acid ester peak for the unaged sample, then decreases as the time at 100°C is increased from 10 days to 30 days to 40 days. In fact this peak was not found in the sample aged 40 days. The preferential loss of the ester of hexanedioic acid during accelerated aging tests is directly related to the fact that it has a higher vapor pressure than decanedioc acid at a given temperature.

Similar trends are observed for the series of samples aged at 70°C, 85°C, 125°C, and 150°C. As might be expected the time required for the intensity of the hexanedioic acid ester peak to decrease in intensity relative to the decanedioic acid ester peak is dependent on the temperature of aging, that is, the higher the temperature the quicker the depletion of the hexanedioic acid ester. This is shown in Figures 32 through 34 where the samples were aged for 2, 4, and 7 days respectively at 125°C. The peak due to the ester of hexanedioic acid decreases rapidly and is not found for the sample aged at 125°C for 7 days.

Figures 35 through 37 show the RICs, acquired using a pyrolysis temperature of 995°C, for samples aged 5, 20, and 40 days respectively at 100°C. It is interesting to note the similarity of the 'fingerprint' patterns of the three RICs between scans 0 and 750. Although pyrolysis of the acrylonitrile-butadiene rubber samples at 995°C gave fragments characteristic of the decomposition of the rubber, the most obvious change in the RICs of a series of samples aged at a given temperature for various periods of time was the loss of the esters of hexanedioic acid which was observed for the samples pyrolysed at both 300°C and 995°C.

The pyr-GC/MS results for both the polychloroprene and acrylonitrile-butadiene rubbers indicate that loss of additives is taking place and the loss is dependent on thermal history. That is, the rate of loss appears to be dependent on temperature and that for a given temperature the depletion of additive increases with time. To utilize this technique to predict lifetime of an elastomer would require both the determination of the temperature dependence of the rate of depletion of the additive and the knowledge that the depletion adversely affected the performance of the rubber. It is less obvious from the pyr-GC/MS results whether or not the level of cross-linking in these elastomers is changing with thermal aging.

3.3.3 Polyisoprene (Natural) Rubber. The RIC of an unaged polyisoprene sample pyrolysed at 300°C is shown in Figure 38. There is one major peak limonene (scan 331), the Diels-Alder adduct of two isoprene (2-methyl-1,3-butadiene) molecules. This pyrogram is typical of the four polyisoprene samples analysed.

The RIC of an unaged sample of polyisoprene pyrolysed at 995°C is shown in Figure 39. There are four major products of the pyrolysis; 2-methyl-1,3-butadiene (scan 53), toluene (scan 133), xylene (scan 212), and limonene (scan 325). Figures 40 and 41 show the RICs of the polyisoprene samples aged 13 days at 100°C and 5 days at 150°C respectively. Unlike the unaged sample where the intensity of the limonene peak was similar to the 2-methyl-1,3-butadiene peak, the major peak in Figures 40 and 41 is the 2-methyl-1,3-butadiene peak while limonene is a minor constituent (scan 317 and scan 315 respectively).

As a result of the small number of samples available for analysis it is difficult to determine if pyr-GC/MS could be used to monitor the degradation of polyisoprene rubber. However, the results obtained with the polychloroprene and acrylonitrile-butadiene samples suggests that the depletion of additives such as plasticizers could be followed with pyr-GC/MS.

4.0 Conclusions

Shore Durometer 'A' hardness measurements, dynamic mechanical analysis and pyr-GC/MS have been completed on oven aged samples of three rubber formulations; polychloroprene, acrylonitrile-butadiene and polyisoprene, received from Admiralty Research Establishment, Holton Heath. All three methods have been shown to give qualitative indications of aging in the rubber samples. Measureable parameters such as hardness, Tan δ, storage and loss moduli and the intensities of additive peaks in the pyrograms in polychloroprene and acrylonitrile-butadiene samples were all found to vary with temperature and time of exposure of the samples. Using a first order approach, the temperature dependence of the rate of change of hardness of the acrylonitrile-butadiene has been determined and suggests that hardness change could be used for lifetime prediction studies. The observed hardness changes are likely related to loss of additives and/or increases in polymer cross-link density, but since these mechanisms appear to occur concomitantly the relative affects of each could not be isolated. Further experiments are necessary to determine if DMA and pyr-GC/MS results can be used to quantitatively predict the lifetime of rubber samples from accelerated thermal aging tests. These experiments would attempt to determine the temperature dependence of the rate of change of the measured property of the polymer and also attempt to separate the effects of aging, such as loss of additives and changes in cross-link density, on the performance of the elastomer. The use of these results would require that an arbitrary acceptance/non-acceptance criterion be established for the change in propeties of the elastomers while in service.

Acknowledgement. We would like to thank Dr. V.C.R. McLoughlin and Dr. B.C. Ochiltree for kindly supplying the elastomer samples studied in this report. These samples were prepared and aged under their direction at the Admiralty Research Establishment, Holton-Heath.

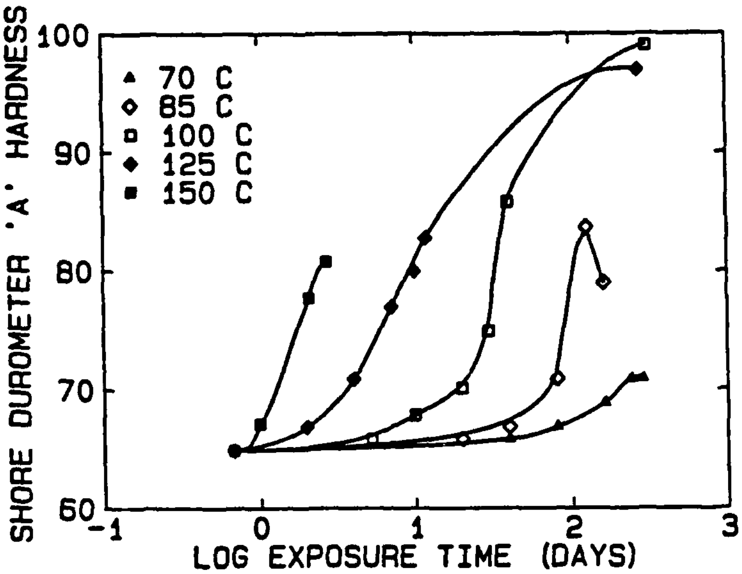

FIGURE 1 - Plot of the hardnesses of acrylonitrile-butadiene rubber samples aged at 70°C, 85°C, 100°C, 125°C, and 150°C against the log of exposure time.

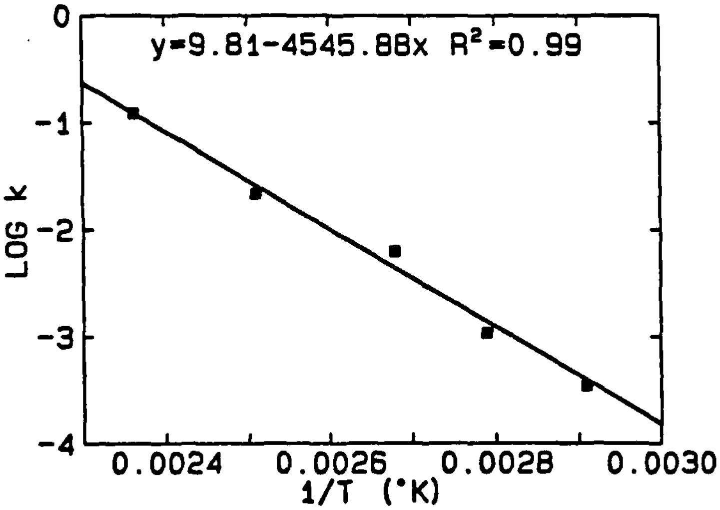

FIGURE 2 - Plot of the log of the rate of change of hardness of acrylonitrile-butadiene samples versus 1/T.

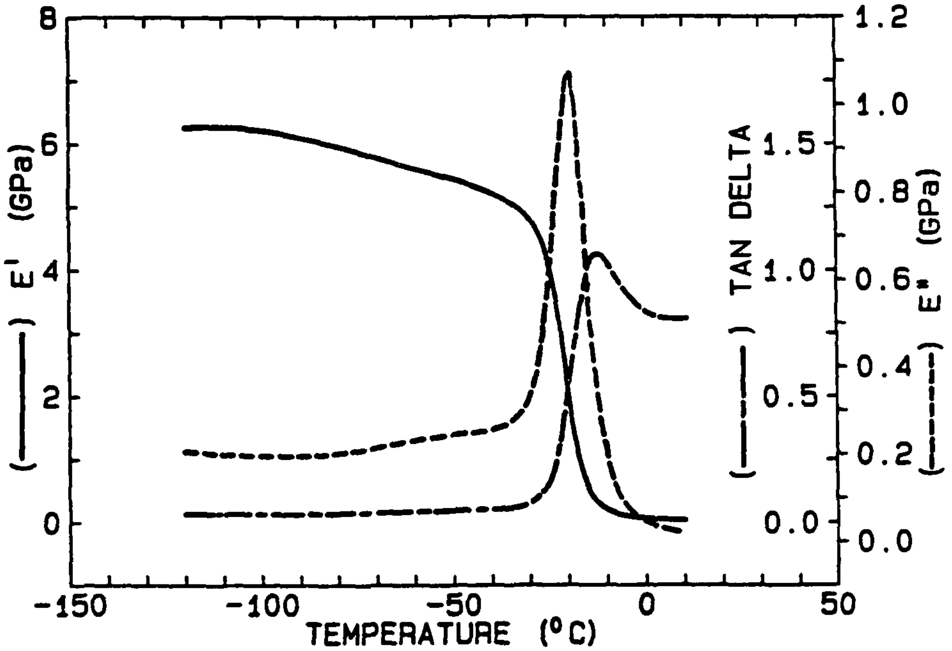

FIGURE 3 - Plot of storage modulus (E´), loss modulus (E´´) and Tan δ versus temperature for an unaged polychloroprene rubber sample.

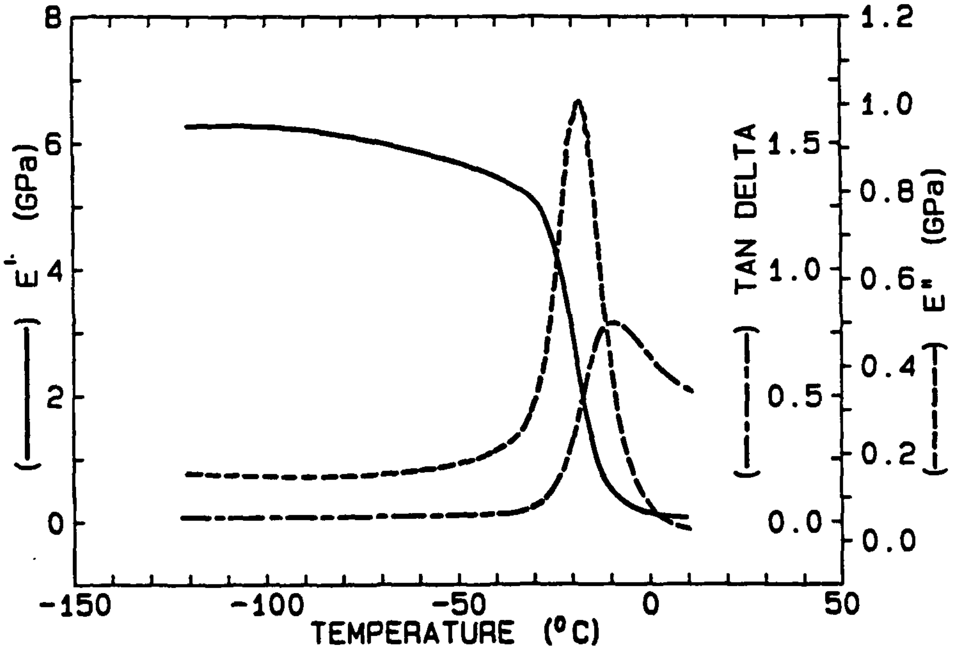

FIGURE 4 - Plot of storage modulus (E´), loss modulus (E´´) and Tan δ versus temperature for a polychloroprene rubber sample aged 20 days at 100°C.

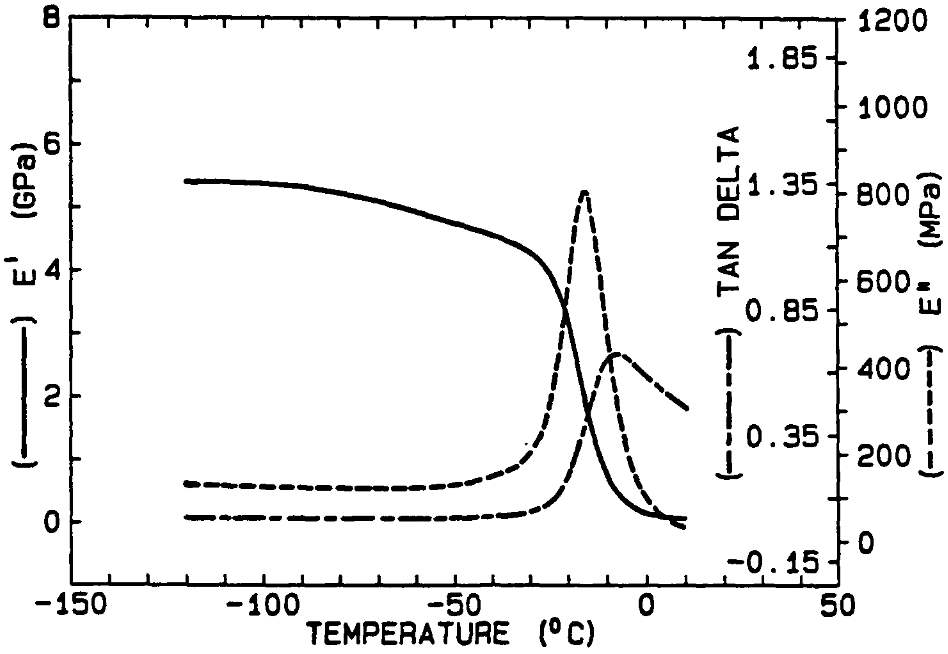

FIGURE 5 - Plot of storage modulus (E′), loss modulus (E′′) and Tan δ versus temperature for a polychloroprene rubber sample aged 40 days at 100°C.

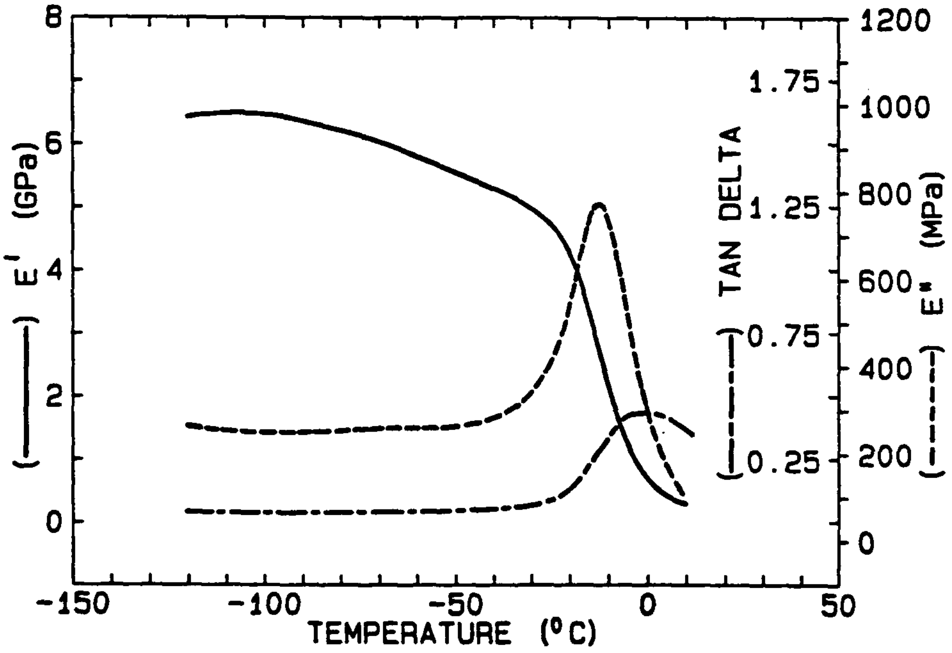

FIGURE 6 - Plot of storage modulus (E′), loss modulus (E′′) and Tan δ versus temperature for a polychloroprene rubber sample aged 83 days at 100°C.

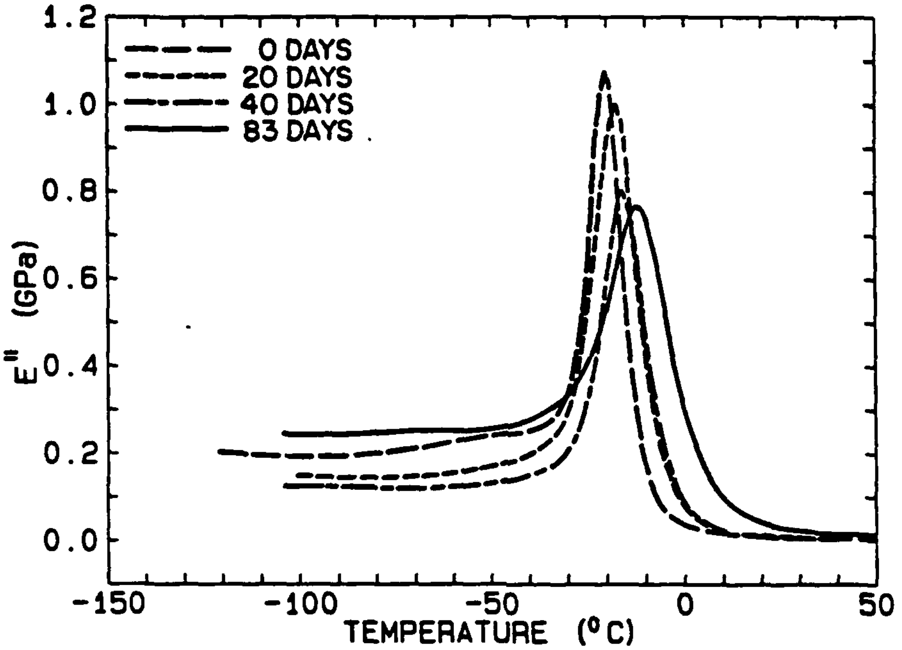

FIGURE 7 - Plot of loss modulus (E´´) versus temperature for polychloroprene rubber samples aged 0, 20, 40, and 83 days respectively at 100°C.

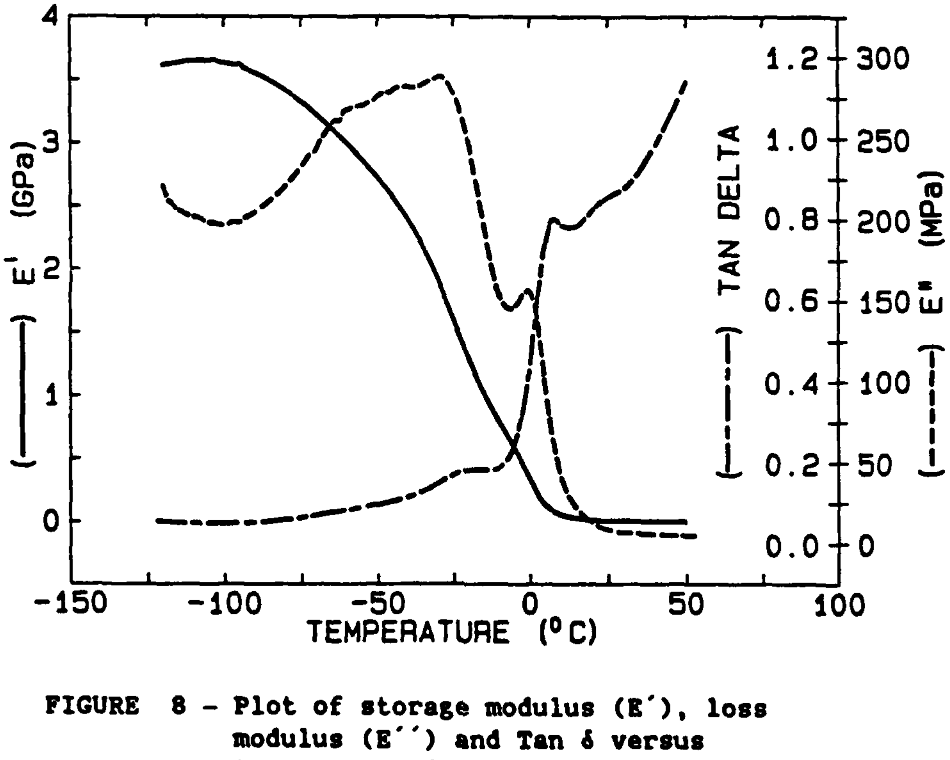

FIGURE 8 - Plot of storage modulus (E´), loss modulus (E´´) and Tan δ versus temperature for an unaged acrylonitrile-butadiene rubber sample.

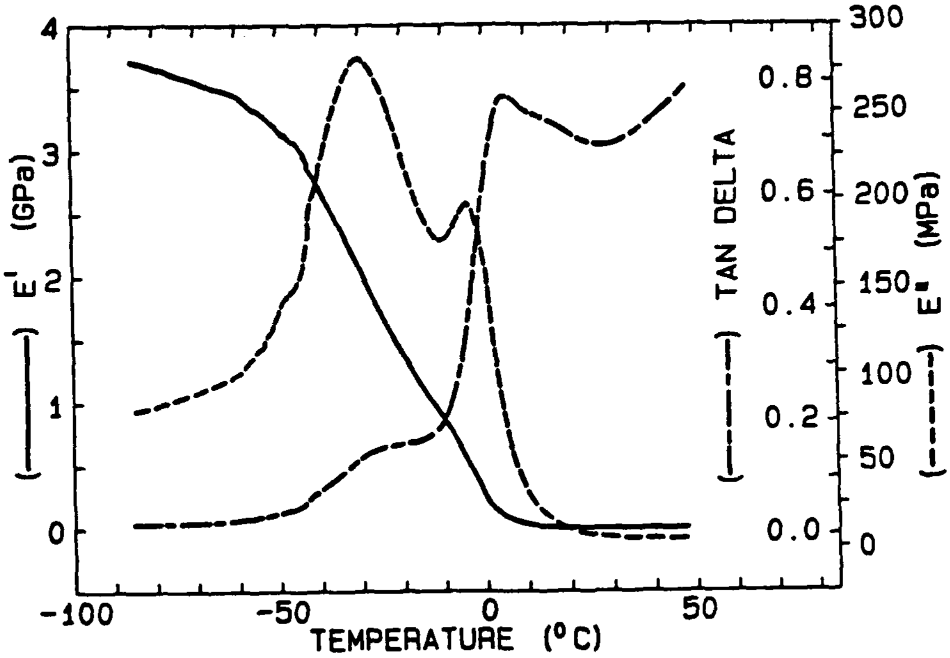

FIGURE 9 - Plot of storage modulus (E´), loss modulus (E´´) and Tan δ versus temperature for an acrylonitrile-butadiene rubber sample aged 10 days at 100°C.

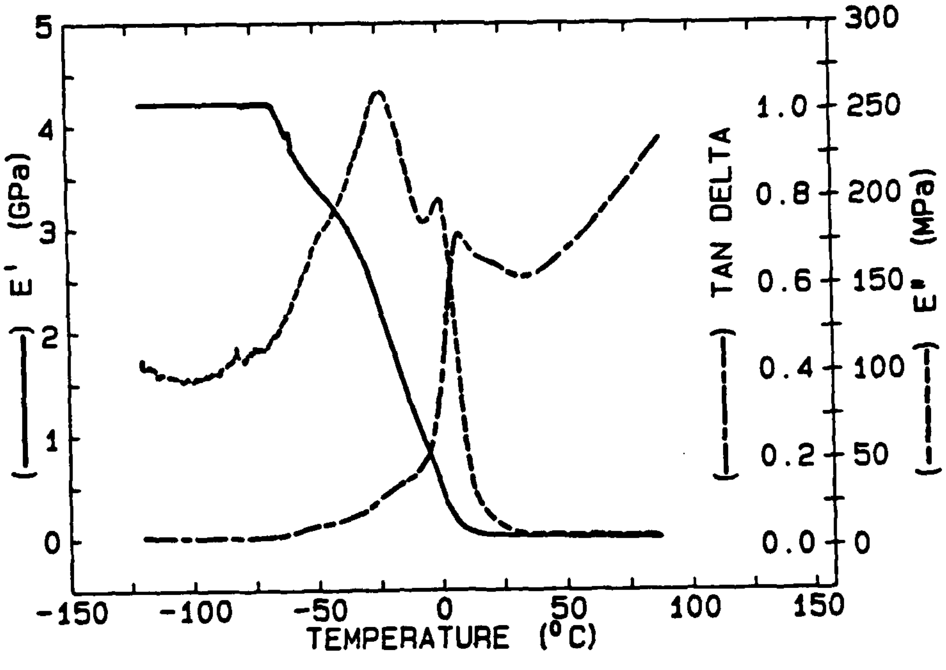

FIGURE 10 - Plot of storage modulus (E´), loss modulus (E´´) and Tan δ versus temperature for an acrylonitrile-butadiene rubber sample aged 20 days at 100°C.

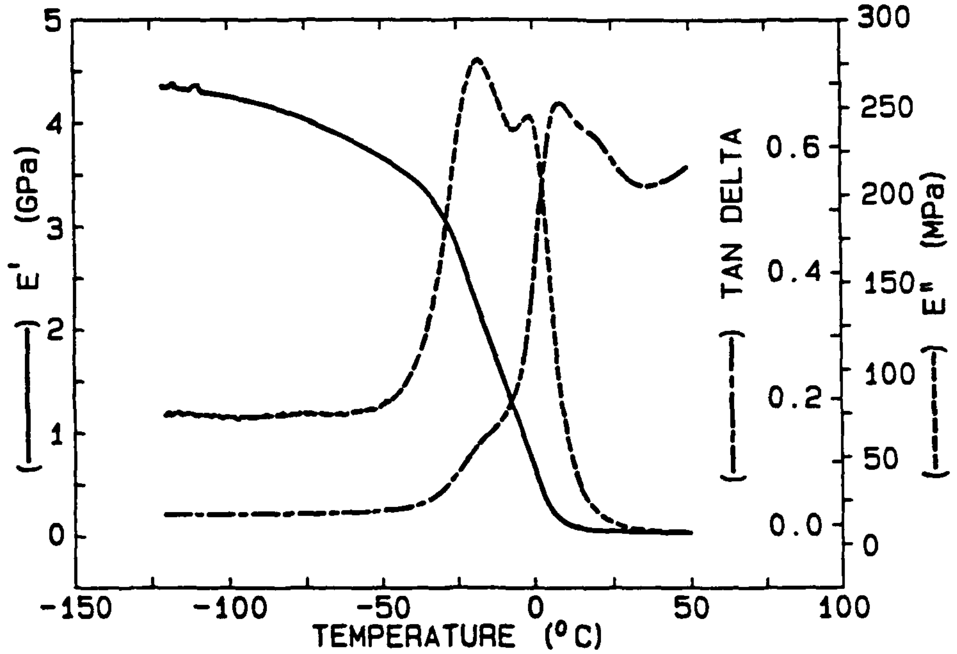

FIGURE 11 - Plot of storage modulus (E´), loss modulus (E´´) and Tan δ versus temperature for an acrylonitrile-butadiene rubber sample aged 30 days at 100°C.

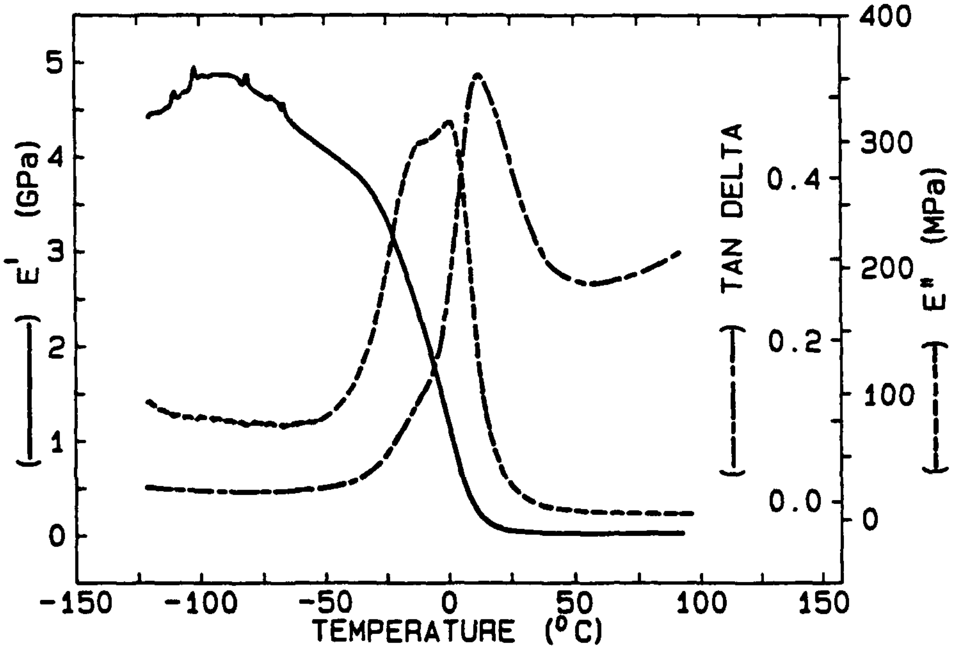

FIGURE 12 - Plot of storage modules (E´), loss modulus (E´´) and Tan δ versus temperature for an acrylonitrile-butadiene rubber sample aged 40 days at 100°C.

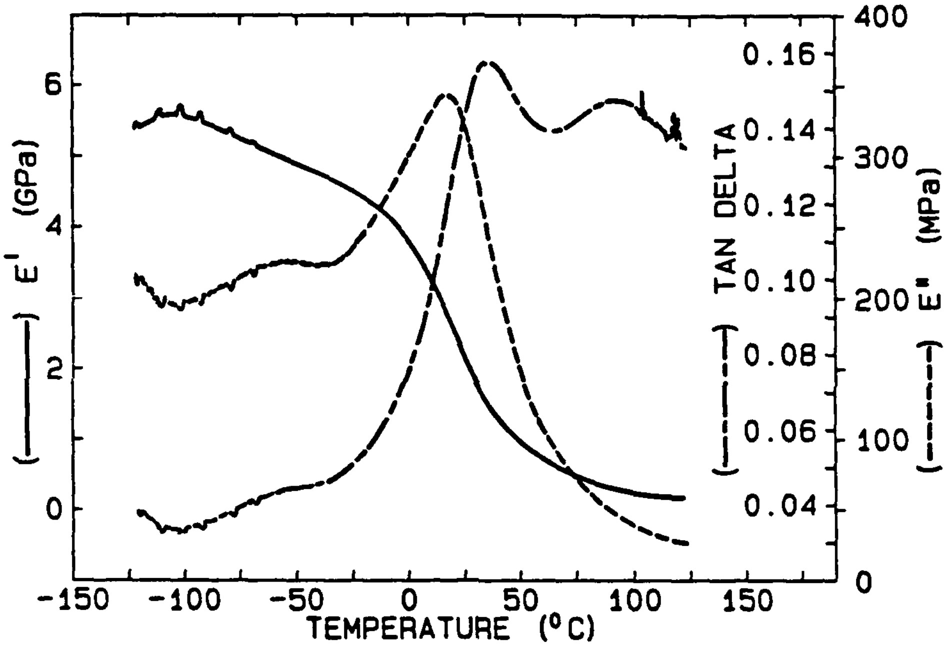

FIGURE 13 - Plot of storage modulus (E´), loss modulus (E´´) and Tan δ versus temperature for an acrylonitrile-butadiene rubber sample aged 300 days at 100°C.

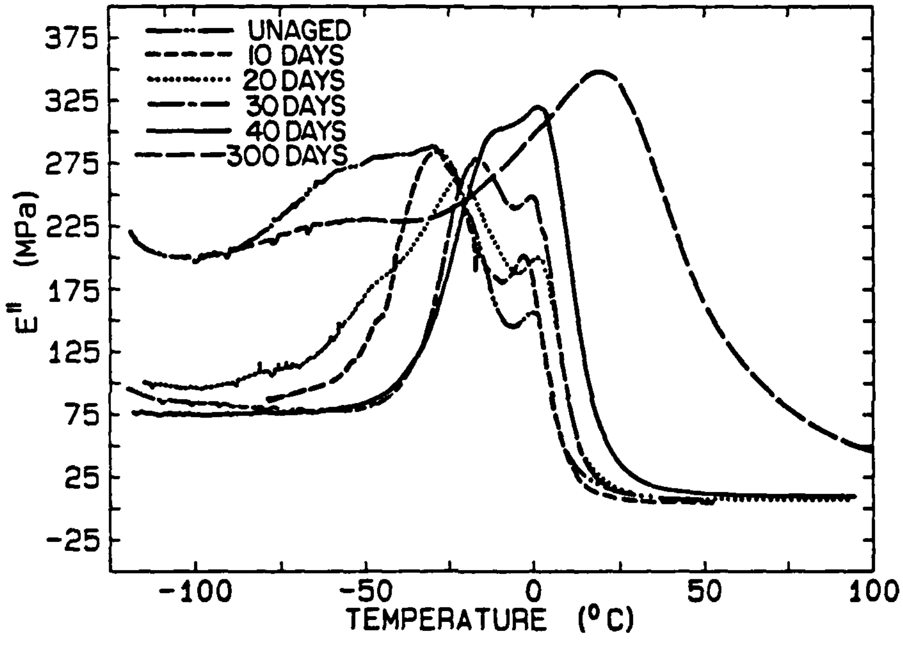

FIGURE 14 - Plot of loss modulus (E´´) versus temperature for acrylonitrile-butadiene rubber samples aged 0, 10, 20, 30, 40 and 300 days respectively at 100°C.

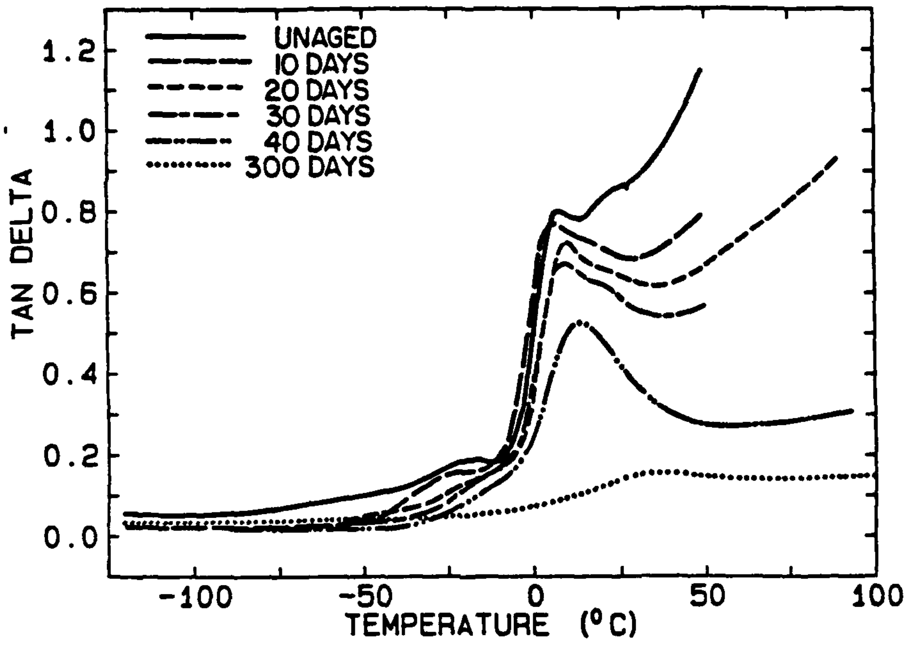

FIGURE 15 - Plot of Tan δ versus temperature for acrylonitrile-butadiene rubber samples aged 0, 10, 20, 30, 40 and 300 days respectively at 100°C.

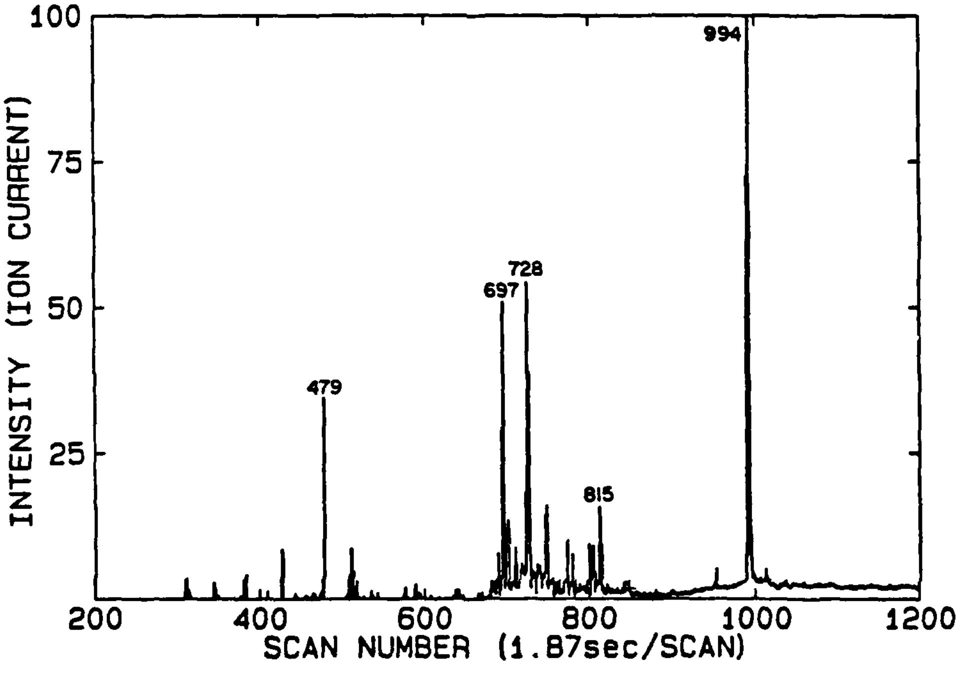

FIGURE 16 - RIC of an unaged sample of polychloroprene rubber following pyrolysis at 300°C.

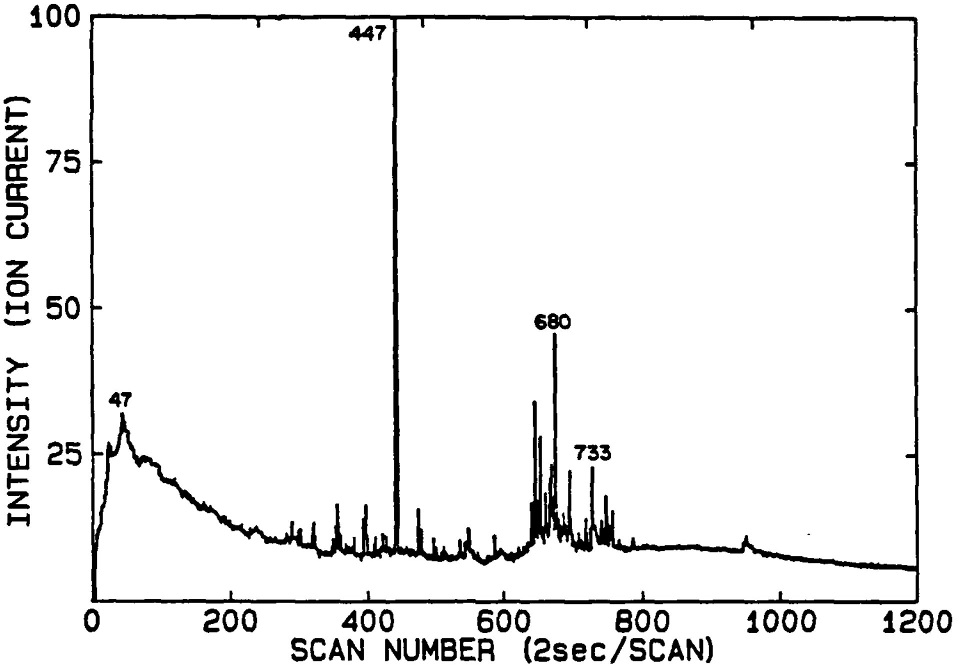

FIGURE 17 - RIC of a sample of polychloroprene rubber aged 30 days at 100°C following pyrolysis at 300°C.

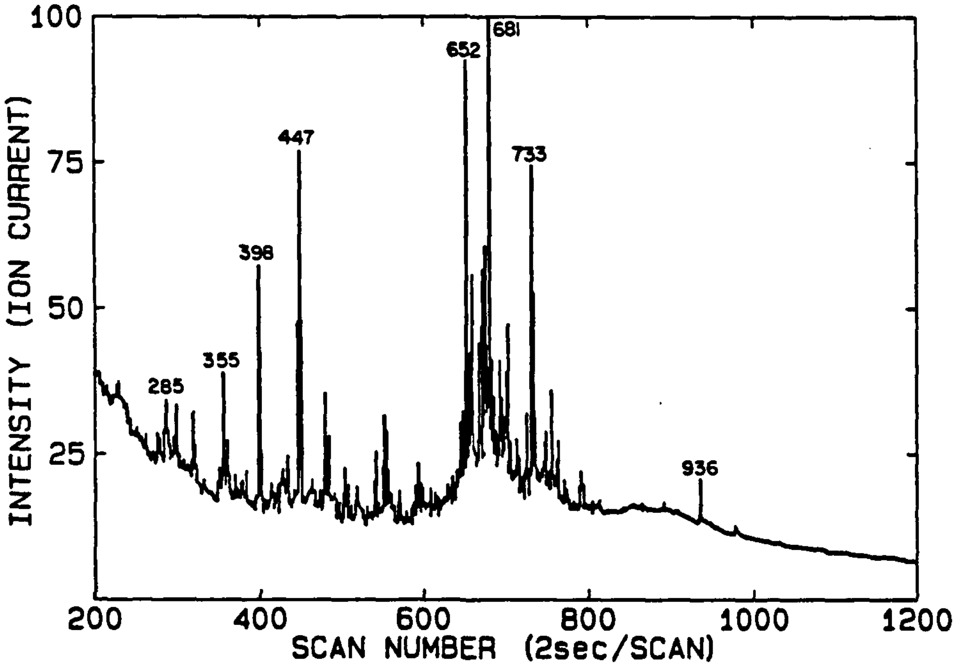

FIGURE 18 - RIC of a sample of polychloroprene rubber aged 40 days at 100°C following pyrolysis at 300°C.

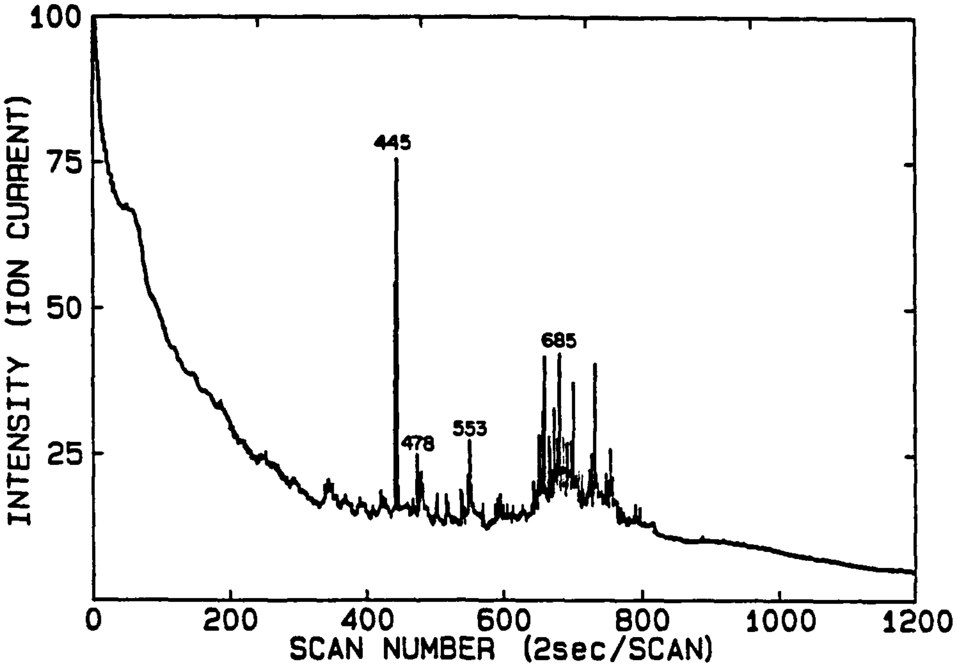

FIGURE 19 - **RIC of a sample of polychloroprene rubber aged 83 days at 100°C following pyrolysis at 300°C.**

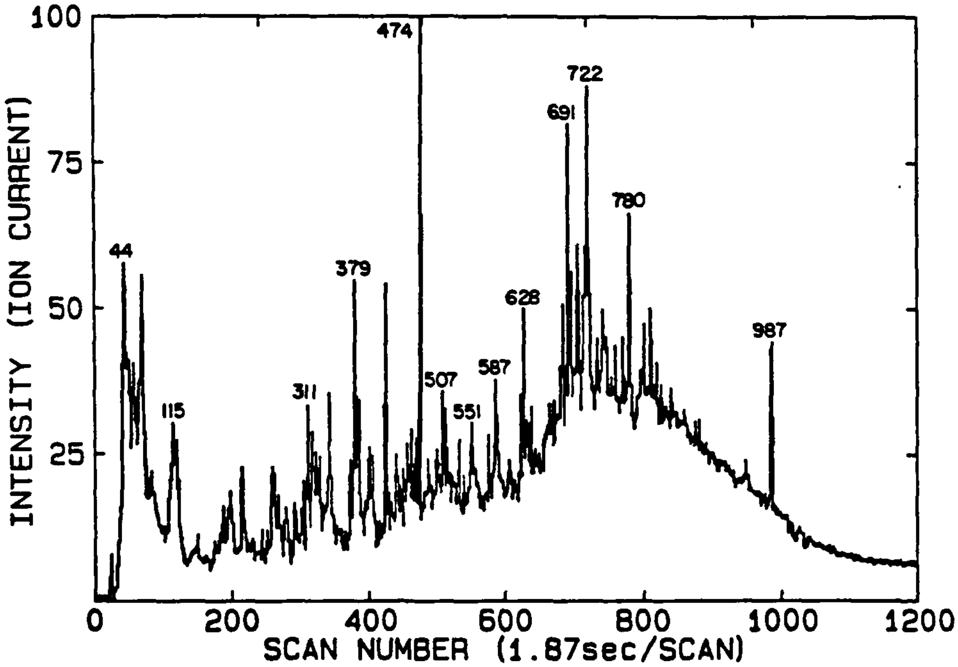

FIGURE 20 - **RIC of an unaged sample of polychloroprene rubber following pyrolysis at 995°C.**

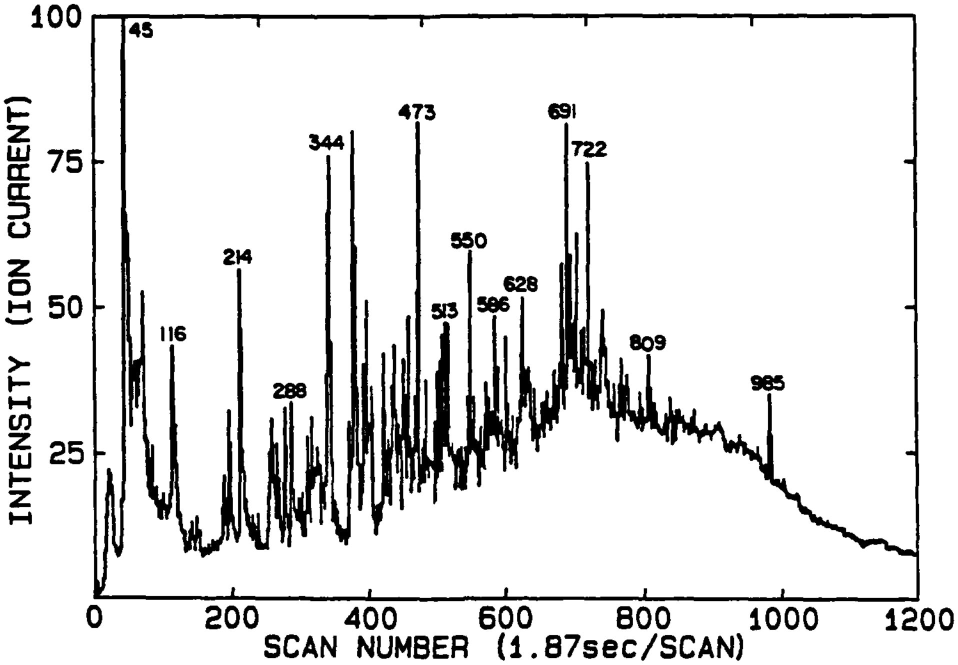

FIGURE 21 - RIC of a sample of polychloroprene rubber aged 20 days at 100°C following pyrolysis at 995°C.

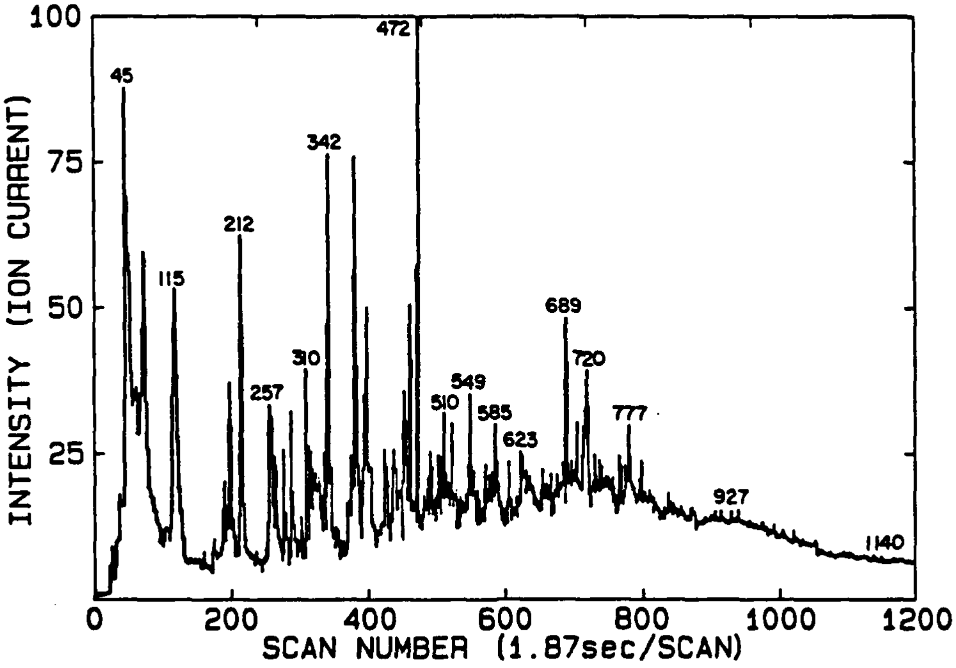

FIGURE 22 - RIC of a sample of polychloroprene rubber aged 30 days at 100°C following pyrolysis at 995°C.

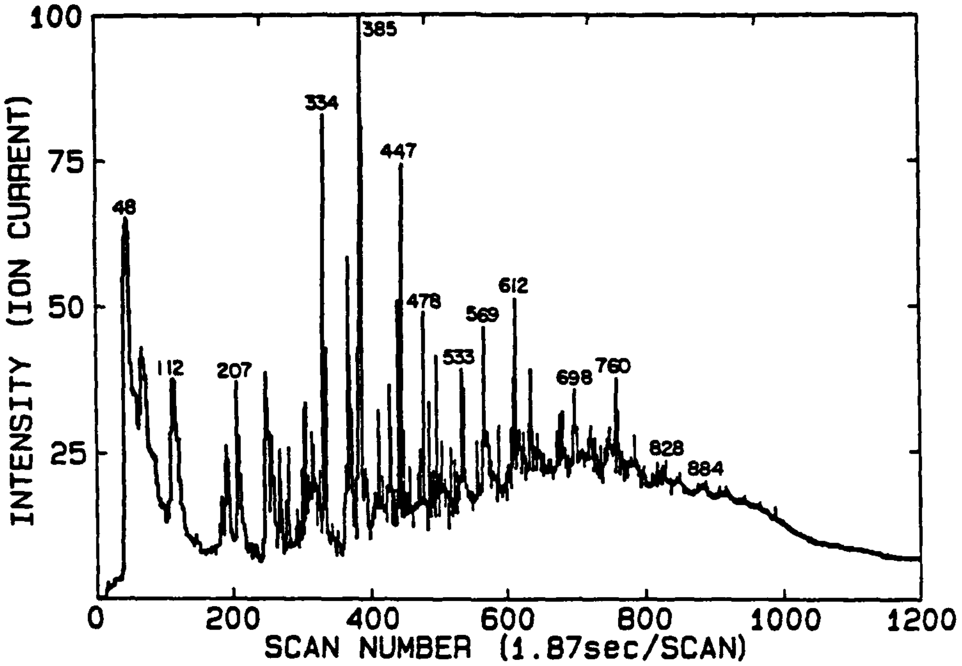

FIGURE 23 - RIC of a sample of polychloroprene rubber aged 83 days at 100°C following pyrolysis at 995°C.

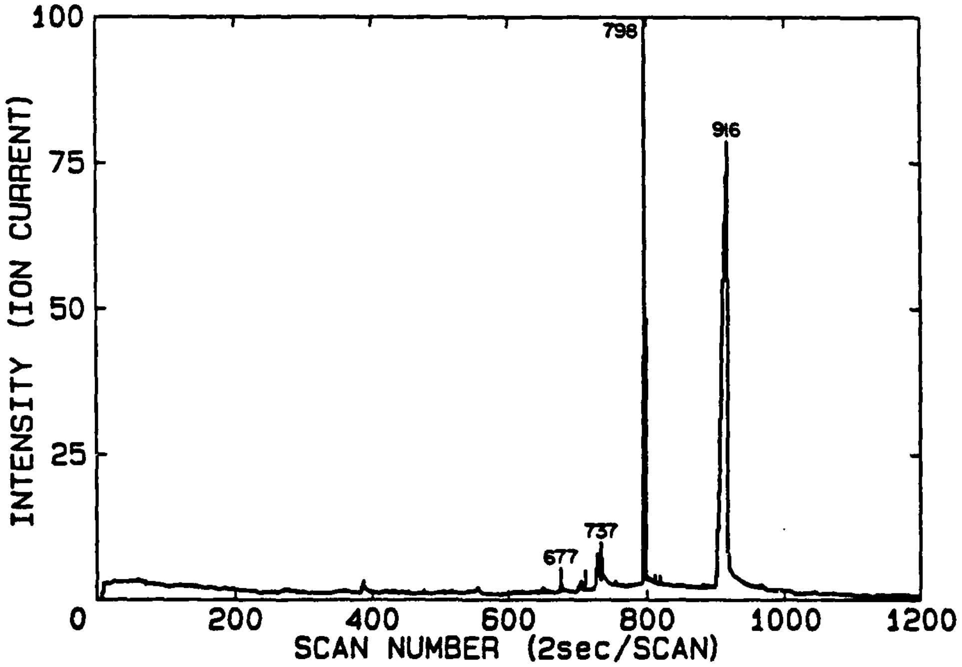

FIGURE 24 - RIC of an unaged sample of acrylonitrile-butadiene rubber following pyrolysis at 300°C.

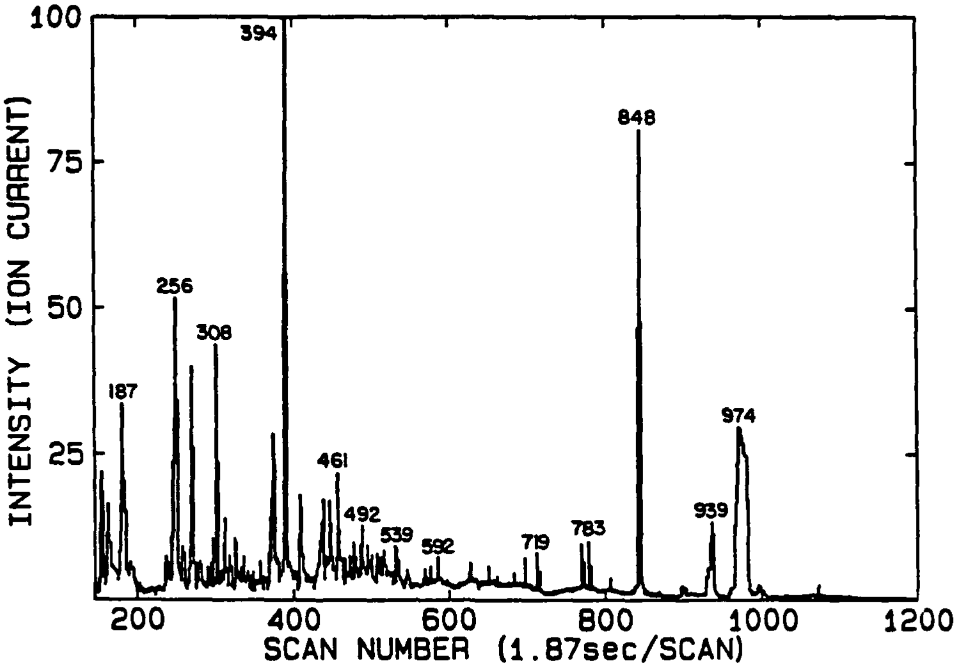

FIGURE 25 - RIC of an unaged sample of acrylonitrile-butadiene rubber following pyrolysis at 995°C.

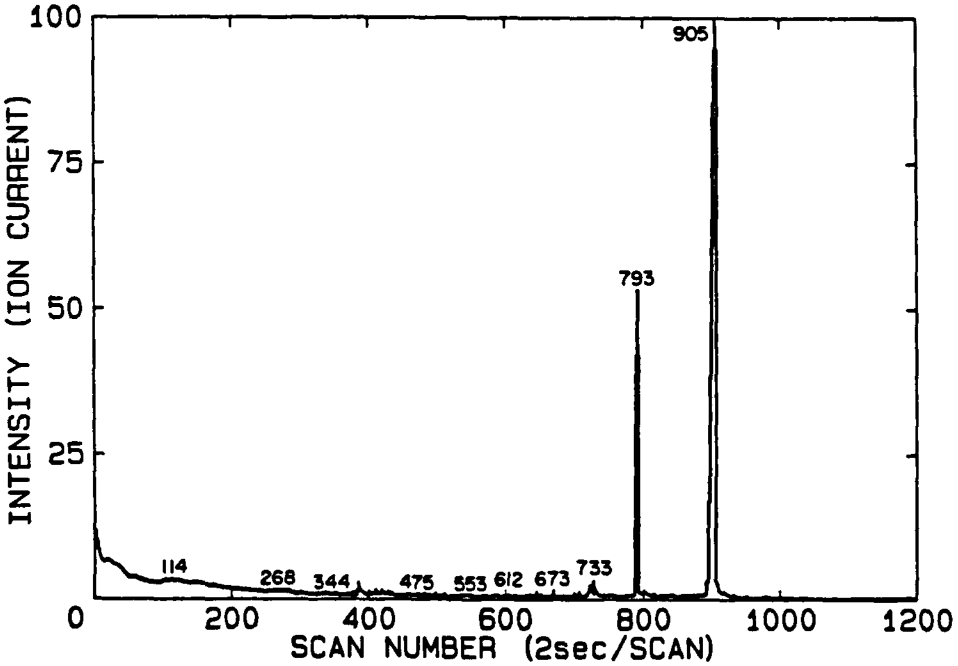

FIGURE 26 - RIC of a sample of acrylonitrile-butadiene rubber aged 5 days at 100°C following pyrolysis at 300°C.

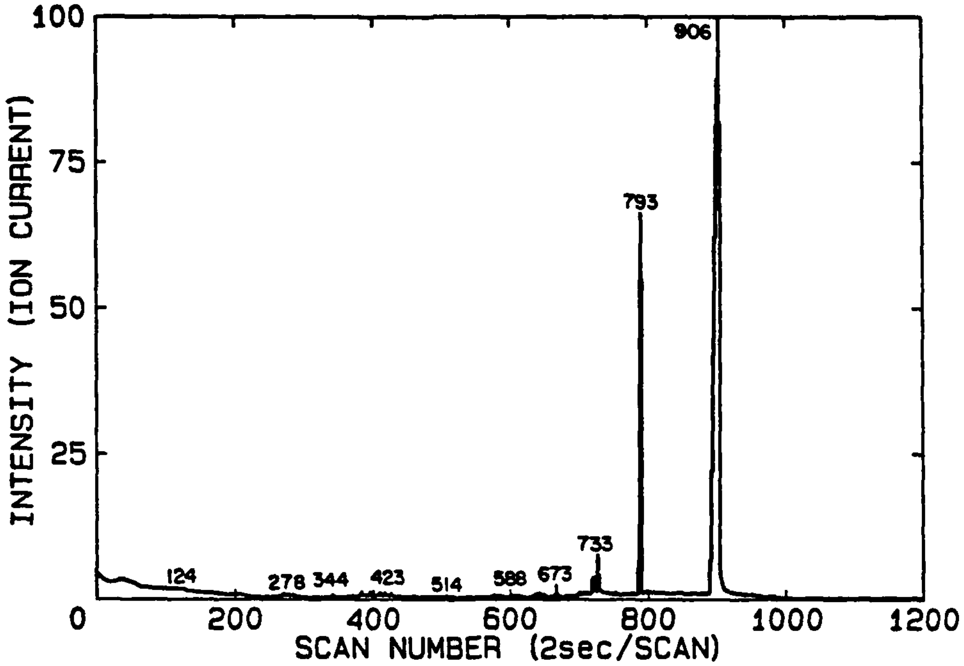

FIGURE 27 - **RIC of a sample of acrylonitrile-butadiene rubber aged 10 days at 100°C following pyrolysis at 300°C.**

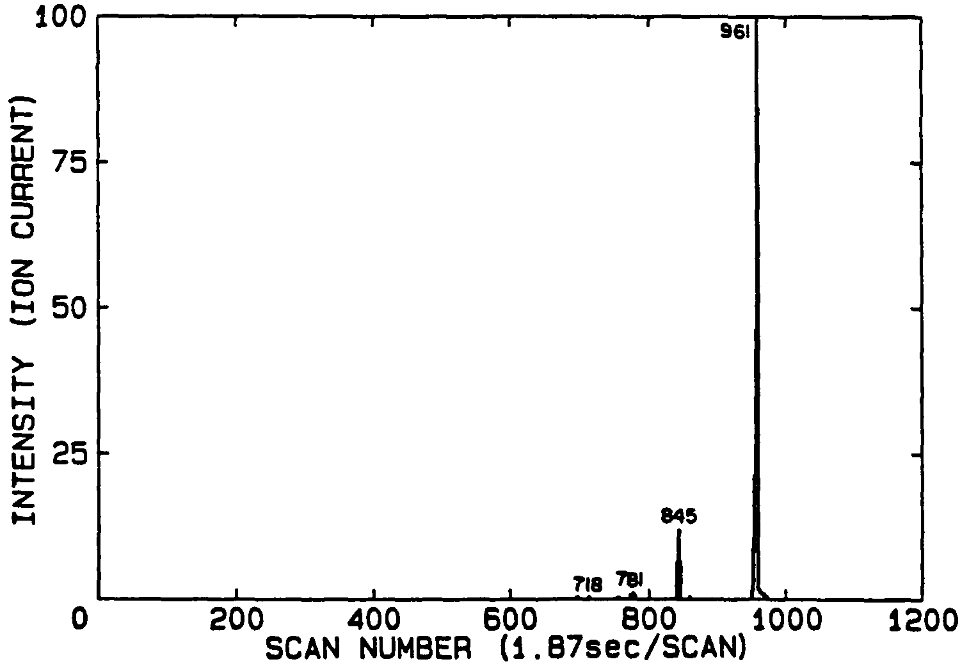

FIGURE 28 - **RIC of a sample of acrylonitrile-butadiene rubber aged 20 days at 100°C following pyrolysis at 300°C.**

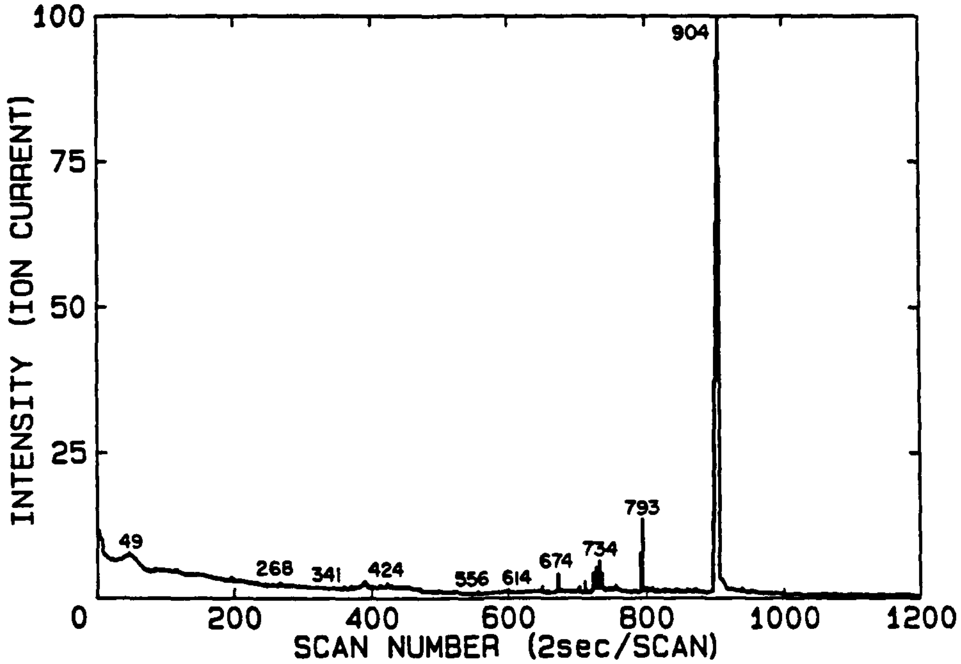

FIGURE 29 - RIC of a sample of acrylonitrile-butadiene rubber aged 30 days at 100°C following pyrolysis at 300°C.

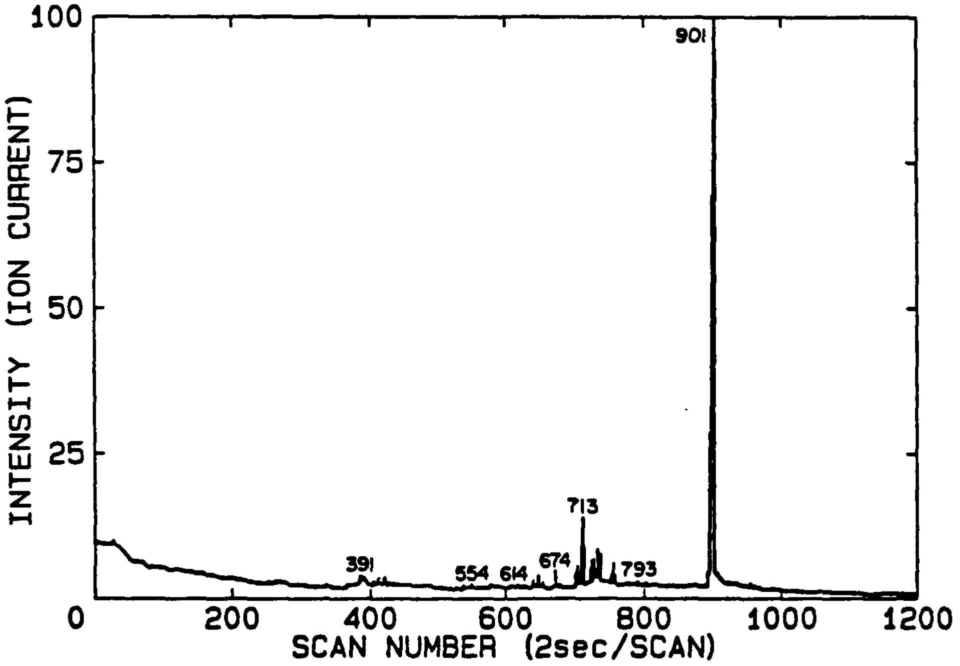

FIGURE 30 - RIC of a sample of acrylonitrile-butadiene rubber aged 40 days at 100°C following pyrolysis at 300°C.

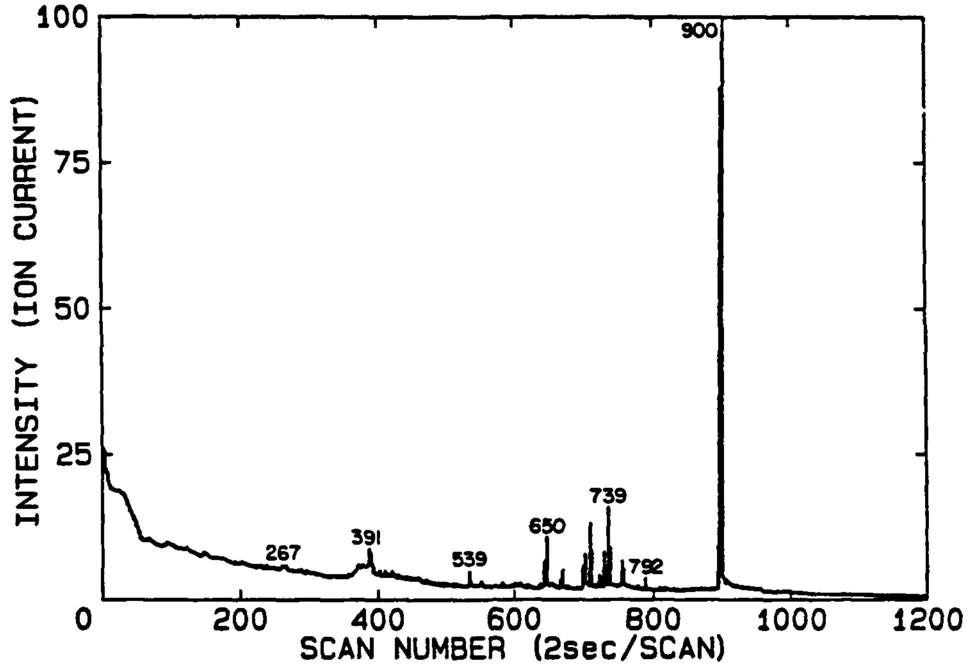

FIGURE 31 - RIC of a sample of acrylonitrile-butadiene rubber aged 300 days at 100°C following pyrolysis at 300°C.

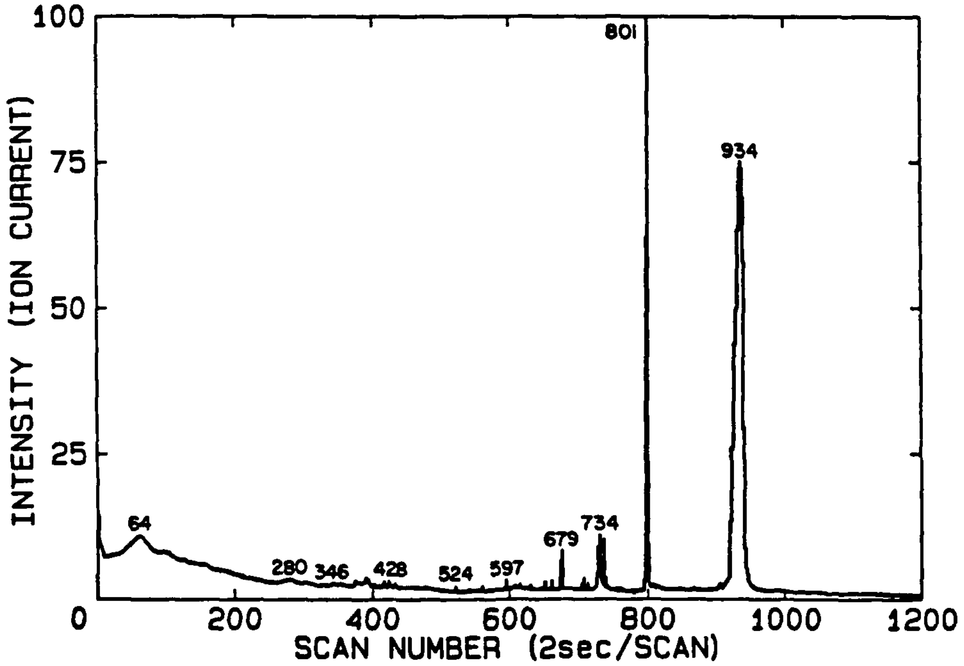

FIGURE 32 - RIC of a sample of acrylonitrile-butadiene rubber aged 2 days at 125°C following pyrolysis at 300°C.

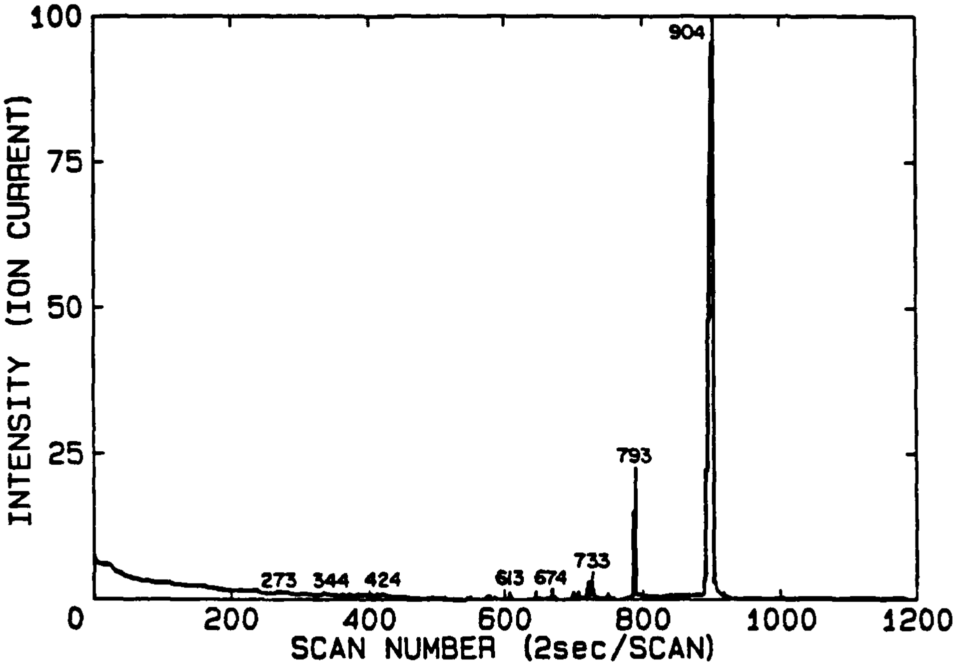

FIGURE 33 - RIC of a sample of acrylonitrile-butadiene rubber aged 4 days at 125°C following pyrolysis at 300°C.

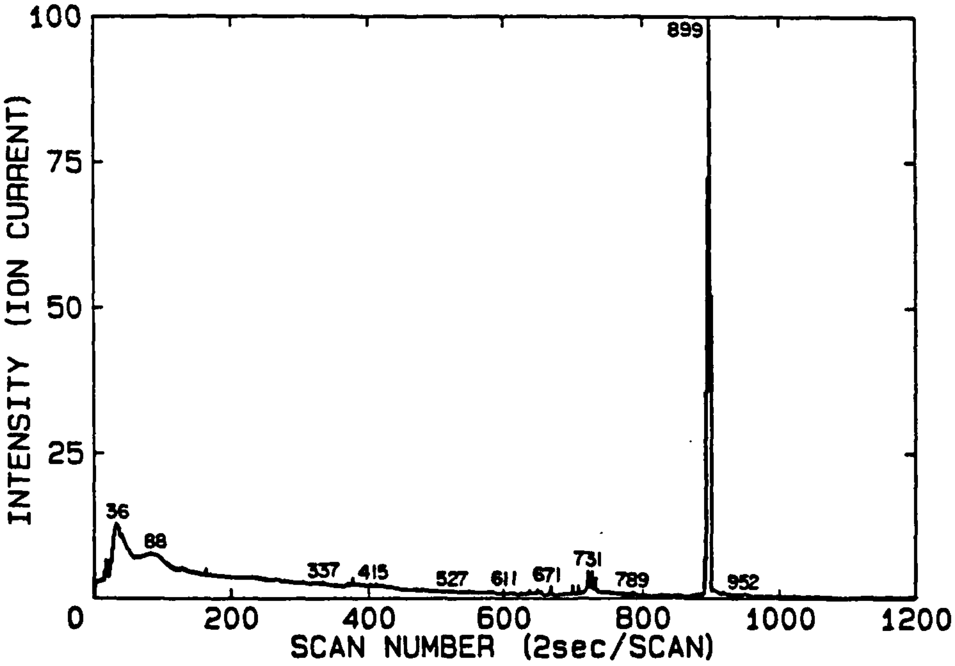

FIGURE 34 - RIC of a sample of acrylonitrile-butadiene rubber aged 7 days at 125°C following pyrolysis at 300°C.

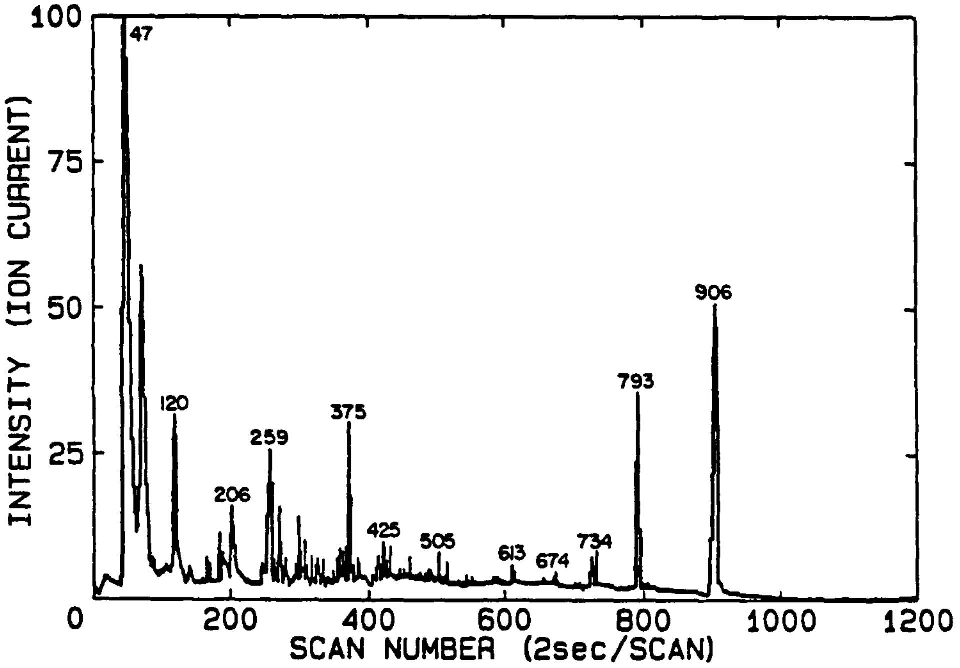

FIGURE 35 - RIC of a sample of acrylonitrile-butadiene rubber aged 5 days at 100°C following pyrolysis at 995°C.

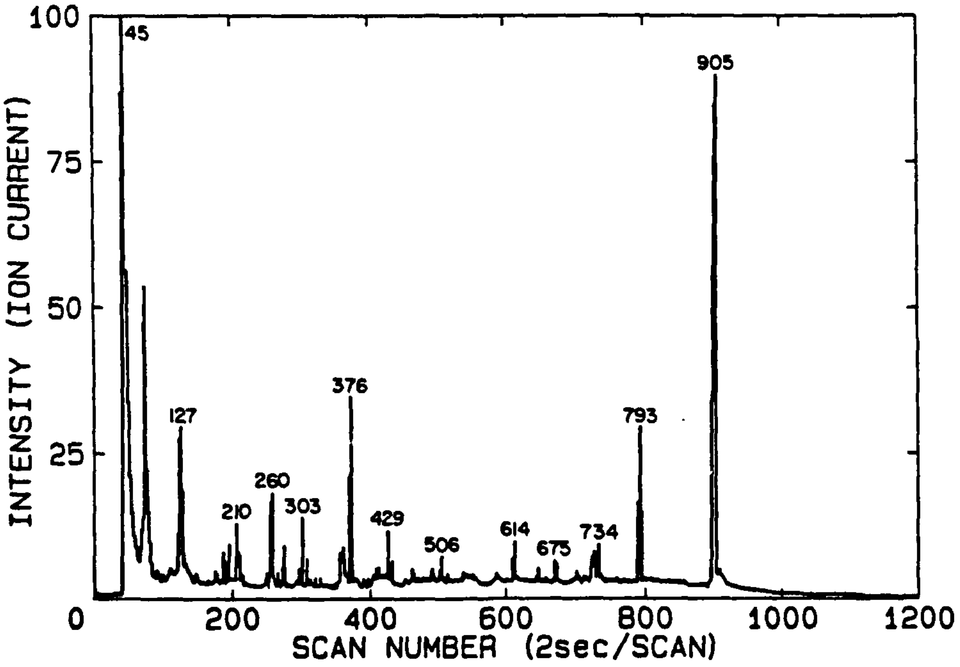

FIGURE 36 - RIC of a sample of acrylonitrile-butadiene rubber aged 20 days at 100°C following pyrolysis at 995°C.

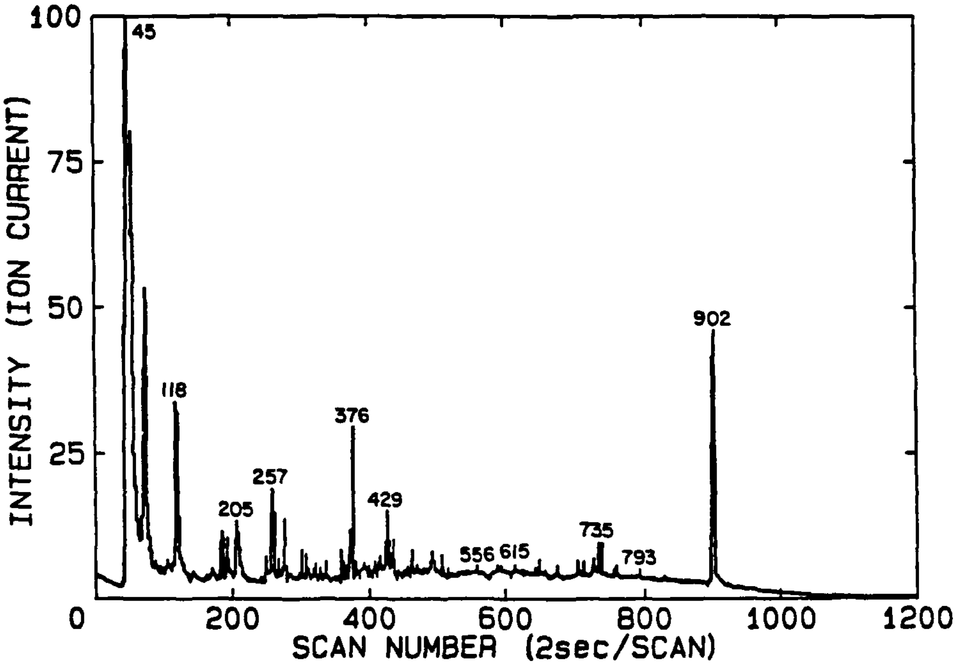

FIGURE 37 - RIC of a sample of acrylonitrile-butadiene rubber aged 40 days at 100°C following pyrolysis at 995°C.

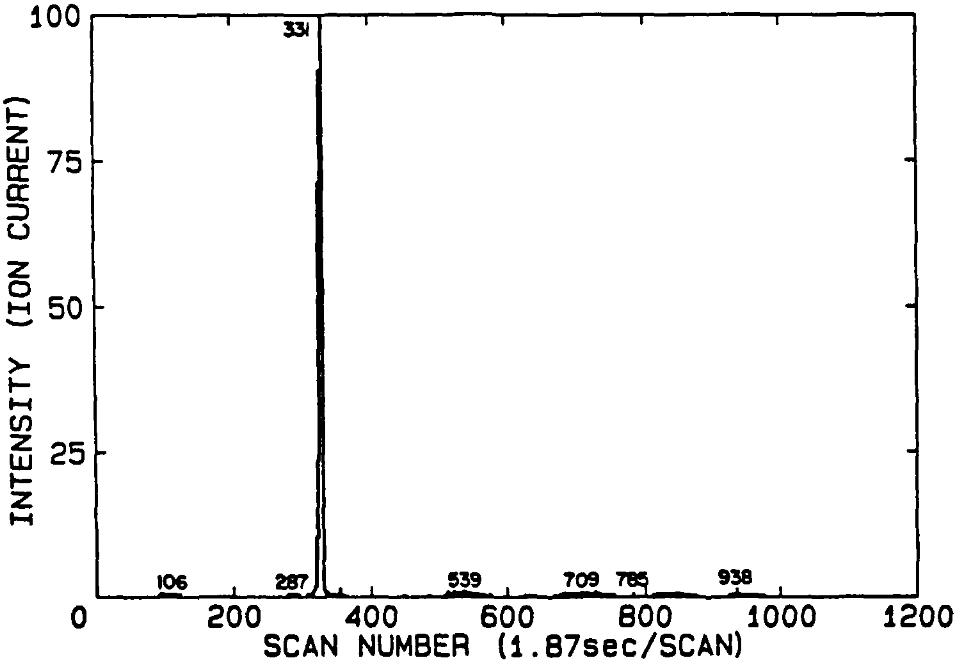

FIGURE 38 - RIC of an unaged sample of polyisoprene rubber following pyrolysis at 300°C.

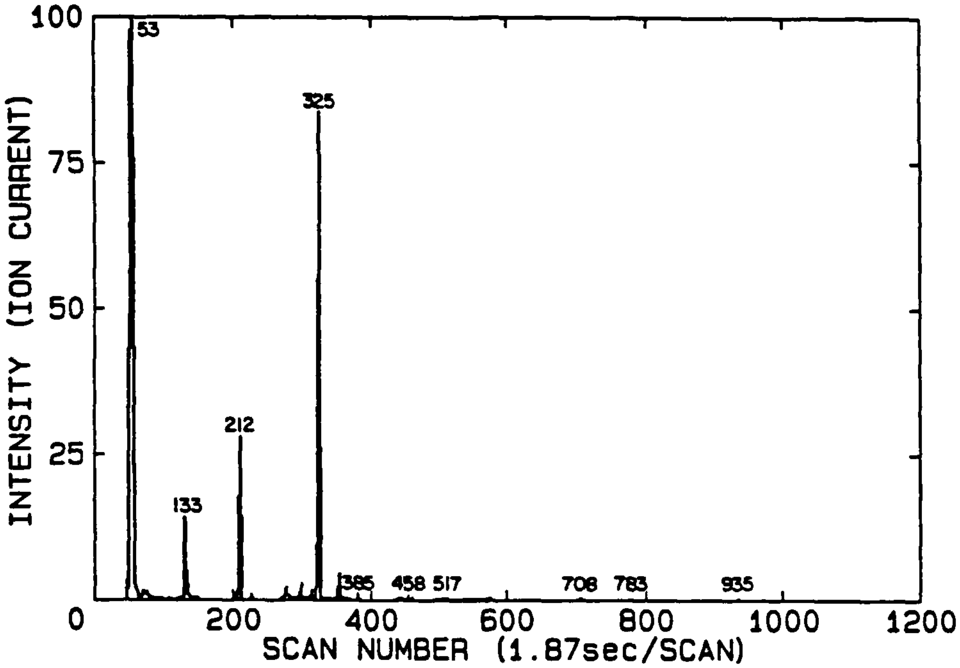

FIGURE 39 - RIC of an unaged sample of polyisoprene rubber following pyrolysis at 995°C.

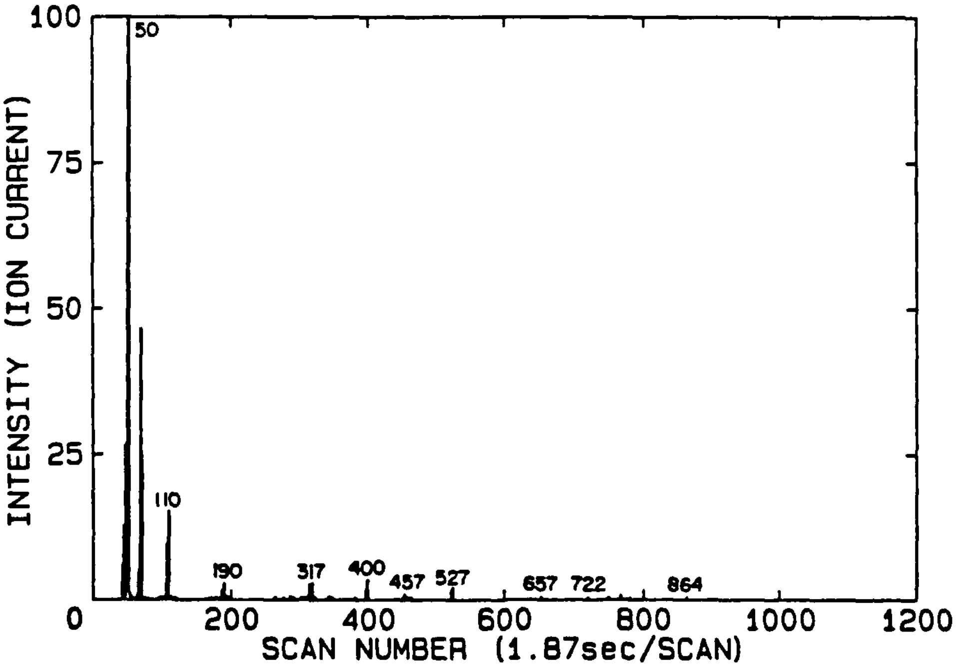

FIGURE 40 - RIC of a sample of polyisoprene rubber aged 13 days at 100°C following pyrolysis at 995°C.

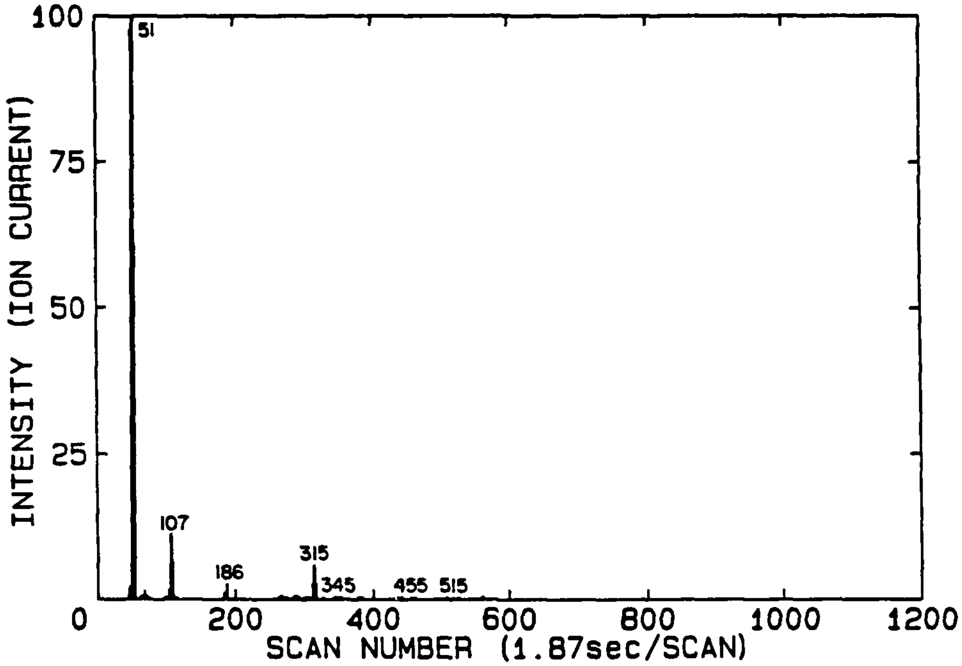

FIGURE 41 - RIC of a sample of polyisoprene rubber aged 5 days at 150°C following pyrolysis at 995°C.

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TAN δ, T_g, GLASS TRANSITION

PYR GC/MS

PLASTICIZERS