

Infrared Spectroscopic Studies of Ultrathin Microtomed Sections of Polymers. Part I. Characterization and Structure Determinations of Cured, Black-Loaded Rubbers

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INTRODUCTION

One of the main drawbacks in the use of infrared spectroscopy for characterization and structure determinations of elastomers has been that carbon black-loaded rubbers containing 50-60 parts of carbon black per hundred of rubber (phr) scatter the incident radiation, and at normal film thicknesses, i.e., 10-15 μ , no transmission occurs.¹

Many attempts have been made to solve the scattering problem. These have included the use of a reflecting microscope attachment for an infrared spectrometer. Unfortunately, preliminary results by Davison² were not substantiated by later work.¹ Removal of the carbon black involves lengthy refluxing with a high-boiling solvent e.g., *o*-dichlorobenzene, with breakdown of crosslinks.³ The use of a filter aid, e.g., Celite, and either filtration through a fine sinter or centrifugation removes most of the carbon black. The resulting solution however, contains polymer which is degraded, oxidized, and hydrolyzed. Thus, reliable

quantitative work on films from this solution is impossible. Another alternative method is pyrolysis of the polymer;⁴⁻⁶ to obtain reliable quantitative information, however, the conditions need to be controlled very carefully. This method, of necessity, degrades the polymer, introducing C=O and O-H groups.

It may be seen from the foregoing discussion that the problem is a difficult one. After a Grubb-Parsons GS3 double-beam infrared grating spectrometer had been set up in these laboratories, a logarithmic potentiometer was fitted to the comb drive to give optical density readings directly on an external recorder. A "scale expansion unit" was inserted between the spectrometer and recorder; this allowed weak absorptions to be expanded electrically. A potential application to examination of black-loaded rubbers was visualized as follows:

(1) Normal film thicknesses for reasonable infrared spectra of elastomers to be obtained are ca. 10 μ . Black-loaded rubber films of these thick

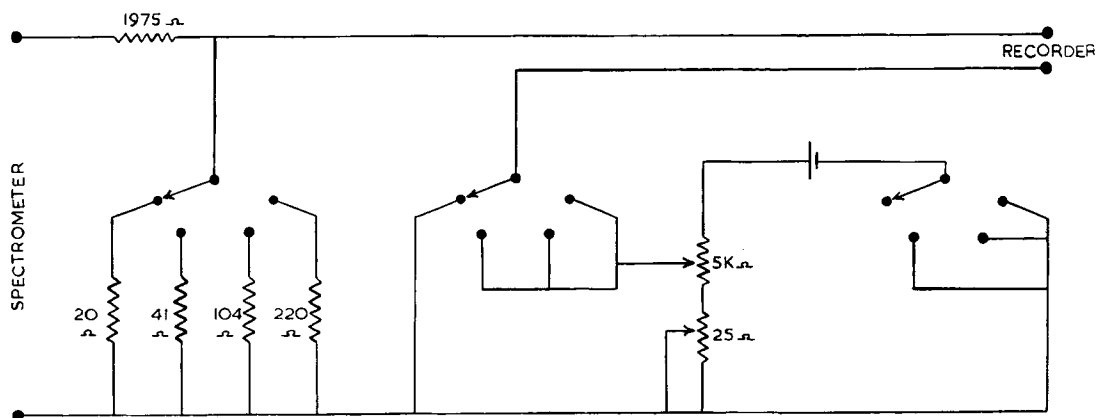


Fig. 1. Circuit diagram of scale expansion unit.

nesses containing 50-60 parts of black (phr) do not transmit detectable radiation in the infrared region (2-15 μ).

(2) If a thinner film is used, e.g., 2 μ (which is the thinnest section of rubber possible by conventional microtoming), and scale expansion is applied, this should give resultant absorptions similar to those of a 10 μ film. However, the scatter would be reduced by a factor of 5^x where x represents the cut-down due to minimizing multiple scatter. It was hoped that x would be greater than 1.

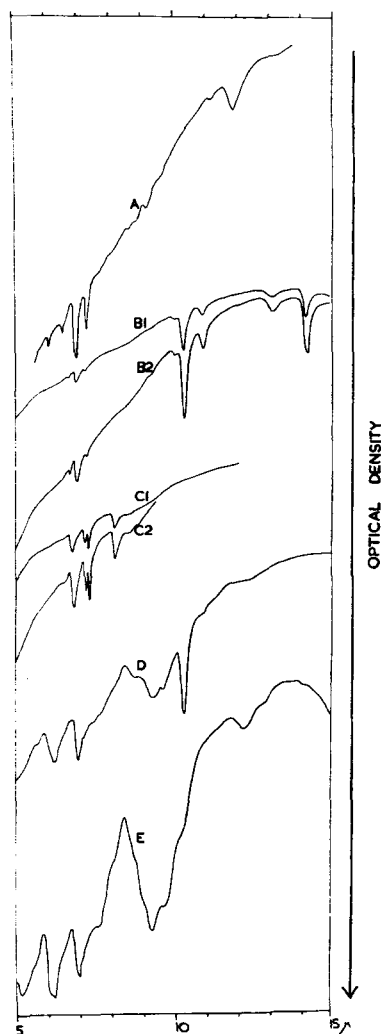


Fig. 2. Infrared spectra of 2 μ sections of reference compounds of black-loaded rubbers (all the compounds contain 50 parts phr of HAF black): (A) natural rubber, scale expansion (2 \times); (B1) butadiene-styrene copolymer (GR-S), normal run; (B2) butadiene-styrene copolymer, scale expansion (2 \times); (C1) butyl rubber, normal run; (C2) butyl rubber, scale expansion (2 \times); (D) butadiene/acrylonitrile copolymer, normal run; (E) neoprene (polychloroprene), scale expansion (2 \times).

EXPERIMENTAL

The instrument used for running the infrared spectra was a Grubb-Parsons GS3 double-beam grating spectrometer with an N.P.L. grating (1200 lines/in.).

A circuit diagram of the scale expansion unit is shown in Figure 1. The d.c. output (0-5 v. for 0-90% absorption) from the logarithmic potentiometer in the double-beam unit of the spectrometer is connected to the expansion unit and then to a Honeywell-Brown recorder (50 mv. full scale sensitivity). The range switch on the expansion unit has four positions; 1 \times , 2 \times , 5 \times , and 10 \times ; these permit expansion of any part of the trace. A dry cell is also included for "backing off" the d.c. standing voltage which exists during scale expansion of parts of the chart display remote from zero. This backing-off device was particularly useful for the scattering, black-loaded rubbers.

Microtomed sections of the black-loaded rubber samples examined, ca. 0.5 \times 1.5 cm. in area and 2-5 μ thick, were cut in petroleum naphtha, toluene, or acetone; the choice of solvent depending on which was needed to swell the polymer sample. The sections were brushed out on pieces of rock salt by means of a blunt "seeker" and a small paint brush. The tendency of the slightly thicker sections to curl up was stopped by sticking down the ends with Sellotape or gripping the ends on the rock salt with Bulldog Clips. The sections were inserted in the sample beam of the grating spectrometer, and gauzes were used in the reference beam to balance out some of the residual scatter. Higher gain than normal was used due to lack of transmission.

Difficulty was encountered in cutting sections of some tire treads due to the addition of crumb, i.e., ground rubber, to the mixes.

RESULTS

Figures 2 and 3 show some of the reference spectra that have been obtained on the recorder for known samples of cured black-loaded rubbers.

Since most common elastomeric materials are polydienes and have characteristic absorptions from 10 μ to longer wavelengths, most of the spectra shown are from 5 to 15 μ , i.e., are run in the first order on the grating spectrometer. It is also easier to obtain good spectra at long wavelengths than at short wavelengths because of reduced scatter (see Discussion).

The use of the scale expansion unit to give amplified absorptions is also shown on several of the spectra.

Figure 4 shows the application to several unknown materials. One stud from each tire tread

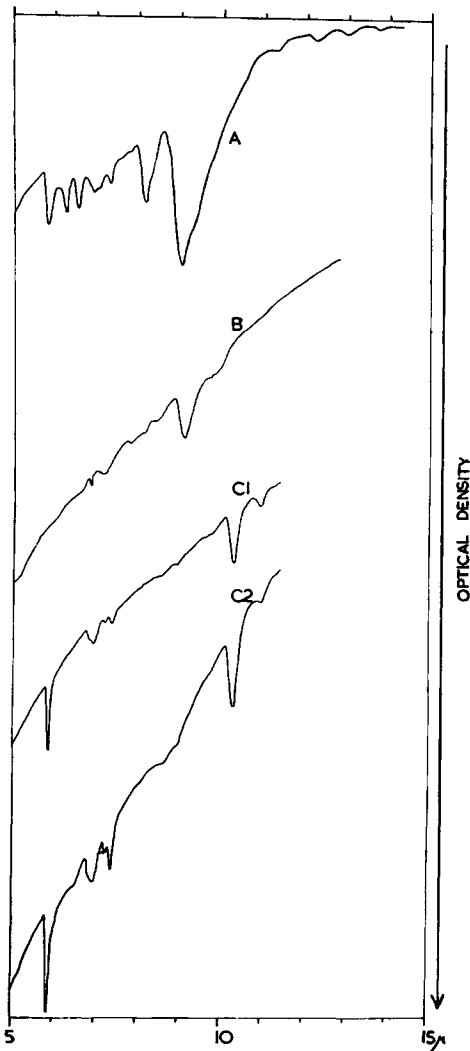


Fig. 3. Infrared spectra of $2\ \mu$ sections of reference compounds of black-loaded rubbers: (A) polyurethan from polytetrahydrofuran and toluene diisocyanate containing 50 parts phr HAF black, normal run; (B) Thiokol/F containing 50 parts phr HAF black, normal run; (C1) butadiene/methyl isopropenyl ketone copolymer containing 50 parts phr Seval Black, scale expansion ($2\times$); (C2) butadiene/methyl isopropenyl ketone copolymer containing 50 parts phr Phil-black A, scale expansion ($2\times$).

provides sufficient sample to characterize the polymer or mixture of polymers present. The structure of the polymer in such samples may also be deduced.

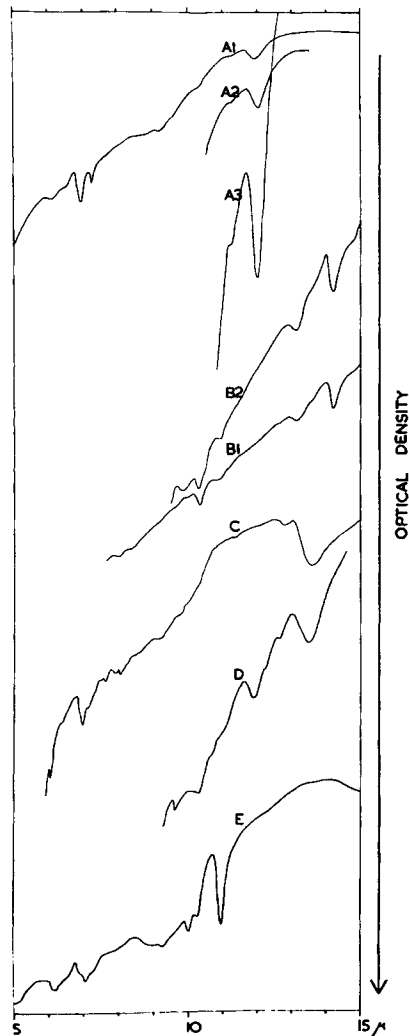


Fig. 4. Infrared spectra of $2\ \mu$ sections of black-loaded rubbers: (A1) earthmover tire tread, normal run; (A2) earthmover tire tread, scale expansion ($2\times$); (A3) earthmover tire tread, scale expansion ($10\times$); (B1) motor car tire tread, normal run; (B2) motor car tire tread, scale expansion ($2\times$); (C) high *cis*-1,4-polybutadiene tire tread compound, scale expansion ($2\times$); (D) 50/50 blend of high *cis*-1,4-polybutadiene and natural rubber tire tread compound, scale expansion ($2\times$); (E) unknown foreign tire casing compound, normal run.

DISCUSSION

By definition, scatter results in the deviation of the radiation from the geometrical path. This may occur (a) primarily at the incident surface (in which case reflection methods may be suitable) or (b) randomly throughout the sample.

Scatter reduces the intensity along the geometrical light axis; the total radiation remains the same but is spread over a solid angle. Both particle size and wavelength λ of the incident radiation

affect the amount and angular dependence of scatter.⁷ For spherical, homogeneous particles of radius r (for $r \ll \lambda/4$), the scatter is proportional to r^3/λ^4 and reaches a maximum for $r = \lambda/4$. For larger particles, the λ^{-4} law is not obeyed, and the scatter is proportional to r^{-1} or to the projected areas of particles.

These considerations refer to dispersions (or solutions) which are sufficiently dilute to prevent multiple scattering. If the concentration of particles is high (as in rubber containing 50–60 parts of carbon black phr), each quantum of radiation will suffer many reflections in traversing the sample, i.e., will undergo multiple scatter, so that the apparent thickness should be much greater than the real thickness. The range of carbon blacks used in rubber varies from 12 to 500 $m\mu$ in diameter, but normal reinforcing carbon black in tread stock, etc., has a diameter of 20–30 $m\mu$. It has been observed by electron microscopy, however, that carbon black particles in rubbers are often arranged in chains ca. five particles in length. Aggregates of carbon black particles and rubber (ca. 2–5 μ across) are also observed with the light microscope.

In the normal infrared region, the wavelength of radiation varies from 2 to 15 μ . If the λ^{-4} law is obeyed, then on going from 2.5 to 5 μ the scatter should diminish by a factor of 16. This is not found experimentally, but scatter does decrease appreciably with increasing wavelength (see Figs. 2–4). In some cases, the backing-off device was used half-way through a spectrum to compensate for this decreasing scatter. Most spectra were run in the 5–15 μ range, as the scatter at very short wavelengths was high.

One possible method of obtaining spectra of black-loaded rubbers directly was to use a reflecting microscope of large numerical aperture which collected a larger proportion of the scattered, transmitted energy. Preliminary work by Davison² at King's College, London, on rubber/carbon black mixes was not substantiated in the studies of cured, black-loaded rubbers performed in these laboratories. The apparent discrepancy between Davison's results and later work in these laboratories is probably explained as follows. Davison's measurements were made on uncured mixes of carbon black and rubber. Adjustment was made for maximum transmission, probably through a window of rubber due to poor dispersion of the black. All our measurements made with a similar reflecting microscope have been on cured

samples in which the black was well dispersed, and this, together with the idea of multiple reflections and aggregate formation, may well explain the differences.

Preliminary work on sections ca. 2, 5, and 10 μ thick of a cured sample of Krylene (SBR rubber) loaded with 50 parts phr of HAF black (particle size 28–34 $m\mu$) showed that infrared spectra with very weak absorptions could be obtained from the 2 and 5 μ sections. These absorptions were amplified by means of the scale expansion unit to give reasonable spectra on the recorder. Thus, the idea of reducing multiple scatter by using ultrathin sections seemed to be a reasonable one. Further work involved the examination of a wide range of polymers containing a range of carbon blacks of different particle sizes. Resultant spectra shown in Figures 2 and 3 show the flexibility of the method. Spectra were obtained of polymers loaded with very fine (e.g., SAF, particle size 14–18 $m\mu$), medium (e.g., HMF-Philblack A, particle size 40–50 $m\mu$), and very coarse (e.g., Seval Black, particle size 250–500 $m\mu$) carbon blacks. It was very much easier to obtain spectra of rubber loaded with coarse carbon blacks. This is not surprising, as the particle size is of the same order as the thickness of the microtomed sections, and "windows" of rubber would tend to occur more frequently.

Later developments of the method were to extend it to examination of unknown materials, mostly parts of tires; however, tubes, conveyor belts, etc., have also been similarly evaluated.

Characterization of polymers as esters, ketones, urethans, dienes, etc., may be carried out from their spectra. Most elastomers are polydienes which give characteristic absorptions due to δCH out-of-plane vibrations in the 10–15 μ region.⁸ These bands, as well as being used to identify polydienes, may also be used to determine relative amounts of 1,2- and 1,4-additions in polybutadienes⁹ and 1,2-, 3,4-, and 1,4-additions in polyisoprenes.¹⁰ Copolymers involving butadiene are readily identified by characteristic bands at ca. 10.0, 10.35, and 11.0 μ (Fig. 2B).

Natural rubber has characteristic absorptions at 12.0 μ due to a δCH out-of-plane vibration of $-\text{CH}=\text{CCH}_3$ groups, and at 7.25 μ due to a δCH_3 vibration (Fig. 2A).

Neoprene (polychloroprene) has a spectrum similar to that of natural rubber except that there is no CH_3 band at 7.25 μ . There are also certain absorptions due to inorganic compounding in-

redients used to carry out the cure, e.g., at ca. $9.25\ \mu$ (see Fig. 2E). These will be dealt with more fully elsewhere.¹¹

Polymers and copolymers of styrene have aromatic absorptions at ca. 6.25 and $6.67\ \mu$, as well as characteristic bands at ca. 13.2 and $14.3\ \mu$ due to pendant monosubstituted benzene rings (Fig. 2B).

A weak, sharp absorption at ca. $4.46\ \mu$ characterizes polyacrylonitrile repeating units in copolymers. This is a little difficult to observe, however, due to a large amount of scatter at the short wavelength end of the spectrum, but may be recognized by using a high value of scale expansion and backing off most of the scatter. The presence of polyacrylonitrile repeating units may be deduced from the absence of other bands in the 5 – $15\ \mu$ region and their influence on, e.g., polybutadiene absorptions: the $11.0\ \mu$ band shifts to $10.85\ \mu$, and the $10.0\ \mu$ band is hardly observable (Fig. 2D).

Butyl rubber is readily identifiable, having bands at ca. 8.16 , 10.55 , and $10.9\ \mu$ as well as a doublet due to $C(CH_3)_2$ groups at 7.2 and $7.33\ \mu$ (Fig. 2C).

Polyketone repeating units in ketone/diene copolymers, e.g., butadiene/methyl isopropenyl ketone copolymer (Fig. 3C), may be characterized by strong absorptions at ca. $5.88\ \mu$. These may be confused with polyacids, but comparison with reference spectra will confirm their identity.

Polyurethans give strong absorptions at ca. $5.8\ \mu$ ($\nu C=O$) and ca. $6.5\ \mu$ (Amide II band) due to urethan groups, as well as aromatic bands at 6.25 and $6.67\ \mu$ due to the aromatic diisocyanates used as chain extenders. The portions due to diisocyanates also have characteristic bands in the 10 – $15\ \mu$ region¹² (Fig. 3A). The identity of the block polymer, e.g., polyester or polyether, used to make the polyurethan may be also deduced from the spectra.¹²

Thiokol F has a spectrum with a broad, strong band at ca. $9\ \mu$ due to ether groups³ (Fig. 3B), S—S bands have low intensity in the infrared region.

Examination of spectra from ultrathin sections of tire treads enables the polymer to be characterized. In Figure 4A, the spectrum of an earth-mover tire tread is typical of natural rubber, the presence of synthetic, e.g., butadiene/styrene (SBR), rubber not being detected.

In Figure 4B, the sections of a motor-car tire tread have spectra characteristic of a butadiene/styrene (SBR) synthetic rubber. It may be concluded that natural rubber is not present, as no absorp-

tion at ca. $12\ \mu$ is shown, even on $10\times$ scale expansion.

Figures 4C and 4D display spectra of tire tread compounds which are respectively, a high *cis*-1,4-polybutadiene and a high *cis*-1,4-polybutadiene/natural rubber blend.

The spectrum of a foreign tire (Fig. 4E) exhibits absorptions characteristic of a polybutadiene containing high 1,2-addition, low *trans*-1,4-addition, and no *cis*-1,4-addition of polybutadiene units, i.e. characteristic of a sodium-polymerized polybutadiene.

In favorable cases, spectra of ultrathin sections of a sample may be obtained within ca. 1 hr. of receipt of the sample. Interpretation takes some time, of course, but when dealing with a limited range of rubbers, the method is capable of speedy results.

Future work¹¹ will describe applications to polymers containing inorganic fillers (with and without carbon black) and also characterization of antioxidants in vulcanized rubbers. The method is capable of being used to characterize unknown materials, process and quality control, and is being extended to the study of vulcanization and rubber/carbon black interaction.

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Synopsis

Previous time-consuming, destructive methods for examination of infrared spectra of cured, black-loaded rubbers have been replaced almost entirely by a rapid new technique which examines the rubber in its original form. By use of ultrathin microtomed sections (ca. 2μ thick) of the rubber and electrical amplification of the absorptions on a recorder quite good infrared spectra of the rubber may be obtained. Characterization and structure determination of the rubber can then be carried out. Many different polymers, copolymers, and mixtures of polymers which have been loaded with up to 60 parts phr of carbon black and cured have been characterized in this way. Typical applications to determinations of polymers in tires, etc. are described. The effect of variation in particle size of carbon black is considered.

Résumé

Les méthodes antérieures d'examen de caoutchoucs étaient longues et basées sur la destruction des polymères en vue de permettre un examen des spectres infra-rouges des caoutchoucs traités et chargés de noir animal; ces méthodes ont été remplacées par une nouvelle technique rapide qui examine le caoutchouc sous sa forme originale. Employant des sections microtomiques ultra-fines, d'environ 2 microns (μ) d'épaisseur, du caoutchouc et agrandissant électriquement les absorptions sur un enregistreur, on obtient de très bons spectres infra-rouges du caoutchouc. On peut alors

effectuer la caractérisation et la détermination de la structure du caoutchouc. Plusieurs polymères différents, des copolymères et des mélanges de polymères qui ont été chargés jusqu'à 60 parties de noir de carbone (pour 100 parties de caoutchouc) et dégradés sont été caractérisés de cette manière. Les applications typiques aux déterminations de polymères dans des pneus etc. sont décrites. L'effet de la variation de la dimension de la particule de noir de carbone est considéré.

Zusammenfassung

Frühere zeitraubende, destruktive Methoden zur infrarotspektroskopischen Untersuchung von vulkanisiertem, russgefülltem Kautschuk wurden fast völlig durch eine rasche, neue Technik ersetzt, bei der der Kautschuk in seiner ursprünglichen Form untersucht wird. Bei Verwendung ultradünner, ca. 2μ dicker Mikrotomschnitte des Kautschuks und durch elektrische Verstärkung der Absorptionen mit einem Rekorder können befriedigende Infrarotspektren des Kautschuks erhalten werden. Damit kann eine Charakterisierung und Strukturbestimmung des Kautschuks durchgeführt werden. Viele verschiedene Polymere, Copolymere und Polymermischungen, die mit bis zu 60 Teilen Russ (auf hundert Teile Kautschuk) gefüllt und vulkanisiert worden waren, wurden auf diese Weise charakterisiert. Typische Anwendungsbeispiele für die Bestimmung von Polymeren in Reifen etc. werden beschrieben. Der Einfluss der Änderung der Partikelgröss von Russ wird untersucht.

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