Fourier Transform Raman Spectroscopy of Elastomers: An Overview⁺

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The application of Fourier Transform (FT) Raman spectroscopy in the field of elastomers has been reviewed. FT Raman spectra of various natural and synthetic elastomers are presented to illustrate both the advantages and the limitations of the technique.

Carbon black and some oils, when compounded with natural and synthetic elastomers, prevent the acquisition of useful Raman spectra. However, all other commercial samples studied produced excellent spectra in the raw and vulcanised states without any sample pre-treatment.

This has allowed quantitative work on blends and isomeric elastomers and also the direct study of the rubber vulcanisation process.

Future developments of the technique are also discussed.

The study of elastomers by Raman spectroscopy has for a long time been a desirable, but highly complex (and hence expensive) technique. Problems associated with fluorescence, exaggerated by the presence of impurities in the elastomer and the addition of crosslinking materials and antidegradants. have meant that the vibrational spectra of elastomers have been mainly limited to infrared spectroscopy. Where conventional Raman spectroscopy has been used materials have been specially selected to be of low fluorescence and have undergone extensive preparation before examination^{1,2}.

This is particularly unfortunate as the technique, with its high sensitivity to the non-polar species (C=C and C-S) which make up polymer chains and the products of vulcanisation, has obvious potential advantages over the complementary technique of infrared absorption spectroscopy.

Recent advances, which combine the use of a near infrared excitation source with Fourier Transform collection techniques³⁻⁵ to produce Raman spectra, have enabled these problems to be substantially reduced, or overcome completely. This has triggered a re-evaluation of the role of Raman spectroscopy in the study of elastomers.

RAW SYNTHETIC RUBBERS

Raw polybutadienes have been successfully studied by conventional Raman spectroscopy⁶, but the time spent in obtaining FT Raman spectra is only a fraction of that required for the conventional technique. *Figure 1* illustrates the quality of spectrum which can be obtained by sampling directly from the bale. Each spectrum was recorded in less than 15 min, including the sample preparation⁷.

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Figure 1. FT Raman spectra of raw polybutadiene rubbers: Intene 50 (A), high vinyl BR (B) and europrene (C). All FT Raman spectra were recorded on a modified Perkin-Elmer 1710 FTIR machine^{20,21} under conditions of 6 cm⁻¹ resolution, 200 scans and 700 mW laser power. The FTIR spectra were recorded using a Perkin-Elmer 1720X Spectrometer.

The $v_{C=C}$ vibration is particularly clear and is sensitive to its environment in a similar way to the $v_{C=O}$ vibration in the infrared. The *cis*, *trans* and vinyl $v_{C=C}$ vibrations, in polybutadiene, can be seen at 1651, 1666 and 1639 cm⁻¹ respectively.

Styrene butadiene (SBR) and nitrile rubbers (NBR) are known to have fluorescene problems. However, *Figure 2* shows that by using that FT Raman technique, good quality spectra can be produced. The styrene and acrylonitrile groups are clearly visible in these spectra. The major feature in the acrylonitrile spectrum is the $v(C \equiv N)$ stretch at 2241 cm⁻¹. It is also interesting to note that the butadiene species is predominantly *trans* in the nitrile rubber (Breon N41.C45).

RAW NATURAL RUBBER

Natural rubber is comprised of repeating isoprene units in the *cis* configuration. Commercial grades of natural rubber have varying amounts of impurities, such as



Figure 2. FT Raman spectra of raw styrene butadiene (Intol 1500) and nitrile rubber (Buna C45.N41).

protein, fatty acids and dirt, which can lead to changes in the appearance of the rubber. These impurities have often resulted in high fluorescence backgrounds or absorption of the excitational source with conventional Raman spectroscopy, making the spectra of these materials difficult to obtain. Similarly the presence of oils, especially aromatic oils, prevents Raman data being obtained conventionally.

As reported previously⁸, different grades of rubber give essentially the same FT Raman spectrum, showing the polyisoprene chain, despite their different levels of impurities and visual appearance (see *Figure 3*). Unlike the polybutadiene rubbers the shift between *cis* and *trans* isomers is, unfortunately, too small to enable the isomers to be resolved. The spectrum of the oil extended natural rubber (OENR 'A') is included here to show that even a black coloured sample, containing large quantities of highly fluorescent material, can give a recognisable spectrum with no prior treatment, although there is a distinct deterioration in spectral quality.



Figure 3. FT Raman spectra of raw natural rubber.

SULPHUR CURED ELASTOMERS

Sulphur Cured Natural Rubber

Sulphur vulcanisation is produced by the reaction of sulphur with an unsaturated polymer chain. Activators and accelerators are used to encourage the production of crosslinks, with a small degree of modification to the polymer chain per crosslink formed. This system of accelerated sulphur crosslinking^{9,10} is used in the vast majority of commercial applications of natural (and synthetic) rubbers.

Accelerated sulphur vulcanisation is classified into three groups according to the ratio of accelerator to sulphur^{9,10}. These are:

- 'conventional' a low accelerator to sulphur ratio;
- 'semi-efficient' approximately equal proportions of sulphur and accelerator;

• 'efficient' – high accelerator to sulphur ratio.

Mechanisms for the process of accelerated sulphur crosslinking have been published. These propose that polysulphidic linkages are initially formed, then, as the cure proceeds, these crosslinks are broken down to form mono- and disulphidic crosslinks. It is also thought that chain modification, such as isomerisation, dehydrogenation, double bond rearrangement (formation of conjugated diene and triene systems) and cyclic sulphide formation, increase as the polysulphidic crosslinks are destroyed and are replaced by mono- or disulphidic crosslinks.

The evidence for this mechanism is, however, only from indirect methods (probe molecules and model chemistry)¹¹. Following this mechanism it is clear that the most efficient cure system is one which accelerates the degradation of the polysulphidic links to mono- and disulphidic crosslinks in such a way as to minimise the production of other main chain modification.

Direct evidence from FT Raman spectroscopy⁸ has confirmed that a greater degree of chain modification (the presence of conjugated diene and triene species) is apparent in both the 'conventional' and 'semi-efficient' cured samples, than in the 'efficient' cured sample, which contains higher levels of accelerator. This is illustrated in *Figure 4*. Bands at 1623 and 1593 cm⁻¹ have been assigned to conjugated species, indicative of main chain modifications and the destruction of sulphur crosslinks. The appearance of these bands with time of cure has also been studied⁸.

One interesting feature of the FT Raman spectra of vulcanised natural rubber systems reported thus far⁸ is the absence of strong

bands in the region 400–600 cm⁻¹. Bands due to $v_{S,S}$ vibrations of poly- and disulphidic crosslinks are expected in this region. The S–S stretch is strongly Raman active and should be apparent even at low concentrations. The fact that no S–S bands are apparent even in the compounded material may indicate that the sulphur is no longer in the S₈ configuration after compounding. Further work on this matter is being continued by the authors as a matter of urgency.

Sulphur Cured Synthetic Elastomers

The vulcanisation of polybutadiene rubber has been studied using conventional techniques¹². The advantages of using the FT Raman technique is that the samples do not have to be extracted or left in the laser beam for extended periods of time to 'burn out'



Figure 4. FT Raman spectra of raw natural rubber (SMR L) and vulcanisates prepared with conventional, semi-efficient and efficient cure systems.

the fluorescence and that there is no restriction on which additives (accelerators, *etc.*) are used.

Other synthetic elastomers (such as styrene butadiene and nitrile rubbers) have also been studied¹³ in rubber blends and during vulcanisation. The blending of different rubbers to make a product of specific physical and chemical properties is a common commercial practice (for example in the manufacture of types). Figure 5 shows the FT Raman spectra of NR/NBR and NR/BR blends raw and vulcanised. Bands characteristic of the two components of the blend are clearly visible in the spectrum. Theoretically, a linear relationship¹⁴ exists between the area of a peak and the quantity of material represented by the peak. This relationship has been explored for liquids¹⁵ and also for a BR/NBR blend¹⁴. A series of NBR and BR blends was mixed with varying compositions. Figure 6 shows the straight line plot of the ratio (area $v_{C=N}/area v_{C=C}$) against the percentage of NBR in the blend. This provides a rapid method of determining the nitrile content in a BR/NBR blend of unknown nitrile content.

THE EFFECT OF FILLERS

The constituents of a commercial vulcanisate can be separated into four main groups:

- elastomer;
- vulcanising system;
- protective agents;
- reinforcing materials and/or plasticisers.

Reinforcing materials improve tear and abrasion properties of the rubber as well as increasing the Young's modulus, hysteresis and creep. The most common are carbon black, silica and calcium carbonate (whiting). FT Raman spectra cannot yet be obtained from samples containing carbon black because of the absorption of the excitation source and subsequent heating of the sample. Different methods to reduce heating in the sample have been attempted but, although the heating effect can be nullified, useful spectra have yet to be obtained. Infrared spectroscopy is similarly limited by the presence of carbon black, especially at reinforcing levels. Special techniques such as photoacoustic spectros-



Figure 5. FT Raman spectra of raw and vulcanised blends.



Figure 6. Calibration curve of percentage NBR vs ratio $v_{(C=N)}$ peak against $v_{(C=C)}$ peak.

copy have been tried but as yet no guarantee of success can be made.

Figures 7 and 8 show the FT Raman and FT ATR-IR spectra of silica and calcium carbonate filled vulcanisates. Both sets of spectra show that the FT Raman spectra do not suffer from the absorptions present in the infrared which are due to the fillers. Polar groups, such as Si–O and C=O, are

not strong in the Raman. Thus, in general, samples may be studied in glass containers with only a slight attenuation of the signal.

PEROXIDE CURED ELASTOMERS

Spectra have been obtained from both natural⁸ and synthetic¹⁴ rubbers crosslinked using dicumyl peroxide (a radical cure



Figure 7. FT Raman and FT infrared spectra of a silica filled natural rubber vulcanisate.



Figure 8. FT Raman and FT infrared spectra of a calcium carbonate filled natural rubber vulcanisate.

system). Modifications in the FT Raman spectra at commercial levels of dicumyl peroxide are slight. When the level of dicumyl peroxide is increased, a comparison of the relative intensity of the $v_{C=C}$ stretch against the v_{C-H} stretching region shows a marked decrease in the intensity of the $v_{C=C}$ band. This indicates a decrease in the efficiency of the higher levels of peroxide where the radical cure system is producing side groups (mainly oxidative) rather than producing C-C crosslinks. These changes are illustrated for natural rubber in Figure 9.

FUTURE DEVELOPMENTS

Despite all of the advances made, so far, in the application of Raman spectroscopy, the main limiting factor in the study of elastomers is the present inability to obtain spectra from samples filled with carbon black. This problem must be overcome before many of the envisaged applications for the technique can become a reality.

Once the problems associated with the presence of carbon black have been solved,

future areas of research into elastomeric materials that become accessible to study by FT Raman spectroscopy are widespread due to the flexibility of the system and the high success rate in obtaining spectra. Continued advancement of instrumental techniques, such as the use of microscopes and the possibility of remote examination with optical fibres, opens new areas to investigation (considerable progress has been made recently in the use of microscopes with FT Raman instrumentation¹⁶ and also in the use of optical fibres¹⁷). Enhancements in resolution, sensitivity and computer software will assist in the investigation of minor changes within a larger chemical structure (as illustrated by vulcanisation chemistry).

Copolymers, elastomer blends and elastomer-thermoplastic blends are useful fields of study by FT Raman spectroscopy. The blending of thermoplastic polymers with elastomers is an area of great interest as the structural and flow characteristics of many thermoplastics have been extensively studied, but those of thermoplastic-elastomer blends is relatively unknown.



Figure 9. FT Raman spectra of two peroxide cured samples of natural rubber.

Quality Control

No raw elastomer has, to date, failed to give a recognisable Raman spectrum with the use of FT Raman spectroscopy. This success rate, coupled with the simplicity and speed of use, could deem the instrument suitable for routine quality control work within manufacturing environments (the FT Raman spectrometer contains a sealed laser system; thus the regulations concerning the use of class 4 lasers do not apply). The use of a computer-based library and spectral matching software removes the need for detailed interpretation.

The availability of such a machine, enabling the rapid checking of elastomers, as well as many of the required additives, before and after compounding or blending would be invaluable in avoiding costly formulation errors and potentially dangerous mismatching of polymers during compounding.

In situ Observations

One problem encountered during vulcanisation is the presence of a temperature gradient across the bulk cure. In such a situation (for example in the manufacture of 'off-road' tyres or rubber bearings) a different cure temperature is experienced throughout the sample, allowing the outermost compound to heat and cool relatively quickly, whilst the inner compound heats slowly but retains the heat for a longer period. If optical fibres were used to sample Raman data at different depths within the compound, this would enable an examination of the different cure reactions and rates within the resultant vulcanisate The cure conditions could then be optimised to give the best cure throughout the whole sample Similarly, this technique could be extended to study in-service ageing This would, for example, allow the study of a large truck tyre in use In such systems temperatures regularly exceed 100° C and results in extended cure, reversion and oxidation reactions The ability to detect how these reactions affect the tyre would enable the development of more reliable tyres with better protective systems.

Latex suspensions give good FT Raman spectra and are a further area for possible application FT Raman data could be used to study vulcanisation reactions in latex suspensions and even follow solution-based polymerisation reactions

Changes in the Raman spectrum of natural rubber during extension¹⁸ and whilst under pressure¹⁹ have been reported and illustrate the feasibility of studying elastomers in stressed states Investigation of elastomers subjected to external physical forces (for example, bridge bearing and flexible couplings) by FT Raman spectroscopy, could lead to a greater understanding of the physical and chemical characteristics of the rubber under these conditions

Orientation effects in elastomers could also be studied Changes in orientation following extrusion from the die (die swelling) may affect the physical characteristics of the rubber

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