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Use of microwave dielectric loss spectroscopy for characterisation of natural rubber/carbon black composites

Laurence Lucchese[1,*], Christopher M. Liauw[1], Norman S. Allen[1], Michele Edge[1,*], Frank Thompson[1], Robert S. Whitehouse[2]

[1] Department of Chemistry and Materials, Faculty of Science and Engineering, The Manchester Metropolitan University, John Dalton Building, Chester Street, Manchester M1 5GD, England; e-mail: l.lucchese@mmu.ac.uk; e-mail: m.edge@mmu.ac.uk
[2] CABOT Technical Centre, Billerica, Massachusetts, USA

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Summary

Microwave dielectric loss spectroscopy (MDS) has shown remarkable potential as a tool for the observation of changes in elastomer network structure within the interphase region of natural rubber/ carbon black composites. During crosslinking (non elemental sulphur system) the dielectric loss progressively increased. However, during ageing at high temperature the dielectric loss decreased. Parallel studies on the unfilled matrix yielded no such variation in dielectric loss. It was therefore concluded that the changes in microwave responses were related to the development of the interphase during curing and its subsequent destruction during ageing. The microwave response was related to the composite mechanical properties as a function of ageing time. The effect of stabiliser was also investigated.

Introduction

Because of its capacity to enhance the physical properties of elastomers, carbon black is used as a reinforcing filler. Its incorporation in natural rubber leads to the creation of an interface between two phases of different conductivity and permittivity. This interface extends a few nanometers beyond the surface of the carbon black and is sometimes described as an interphase. The influence of the carbon black on the thermal-ageing of elastomers is shown in the literature to be dependent on the cure system used (1). Several techniques (2), such as measurement of tensile properties and solvent swelling as a function of ageing time, can be employed to evaluate the deterioration of physical properties, which are the consequence of chemical changes within the network structure of the bulk matrix and the interphase region (i.e. chain scission and destruction of crosslinks). These latter techniques examine only the macroscopic properties of the composite. However the use of dielectric measurements at high frequency enables the investigation of these effects at a molecular level (3). Dielectric methods determine the rotational mobility of dipoles in the presence of a force created by an electric field. Few studies employing microwave dielectric loss methods on elastomer/ carbon black composites appear in the literature. Schneider et al (4) measured the dielectric constants and dielectric losses of

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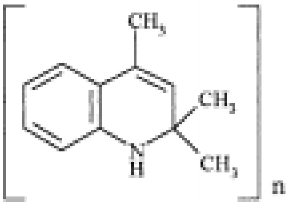
[*] Corresponding author

neoprene loaded with 50 phr of channel black, over a wide range of frequencies, 100 Hz to 3 GHz and at three temperatures, 20, 40 and 60°C. Hanna et al (5) also investigated the dielectric properties of neoprene as a function of frequency, 1 kHz-40 MHz, when mixed with different carbon blacks. They suggested that carbon black provides interfaces and charge carriers resulting in an increase in permittivity. Younan et al (6) studied the electrical and physical properties of ethylene-propylene-diene monomer rubber (EPDM) combined with a semi-reinforcing furnace black over the frequency range 100 Hz-10 MHz. The sharp increase in dielectric properties, at high concentrations of carbon black, was attributed to the interaction between the rubber and the filler. The effect of thermal ageing (90°C) of these composites on the dielectric properties was also investigated and were found to decrease at high concentrations of carbon black (above 50 phr). These investigations only included samples which had lost a maximum of 10% of their initial tensile strength.

The aim of the study reported here is to explore for the first time microwave dielectric loss spectroscopy as a means to monitor the changes in the dielectric properties of filled elastomers during thermal degradation. These properties will be related to changes in tensile properties and solvent swelling.

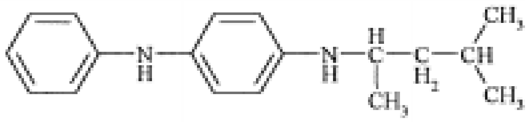
Experimental

Materials Natural rubber (SMR5) and furnace grade of carbon black, Sterling SO (N550), were supplied by Cabot USA. The curatives used for vulcanisation i.e., zinc oxide, stearic acid and tetramethylthiuramdisulphide (TMTDS) were provided by Robinson Brothers Ltd UK. The stabilisers Agerite Resin D and Santoflex 13 were supplied by Vanderbilt and their structure along with their CAS name are displayed below :



Agerite Resin D

Polymerised 1, 2-dihydro-2, 2, 4 trimethylquinone



Santoflex 13

N-(1, 3-Dimethylbutyl)-N'-phenyl-*p*-phenylenediamine

Rubber samples Mixing of natural rubber, carbon black, curatives and antioxidants was carried out at 50°C in a Brabender W50-E mixing chamber with cam blades fitted to a Brabender Plasticorder using a rotor speed of 50 rpm. The mix was discharged from the Brabender chamber and sheeting off was carried out using a laboratory 6"x 12" two roll mill at room temperature set to a friction ratio of 1.16/1. The sheets were moulded/crosslinked at 150 ± 1°C using an electrically heated press. The time for curing was determined using a Monsanto oscillating disc rheometer set at ± 3 degrees of arc. The level of cure was deduced from the torque obtained with the Monsanto as described in the following equation :

$$\%\text{cure} = \frac{T_x - T_{min}}{T_{max} - T_{min}} \times 100$$

where T_{max} is the maximal torque, T_{min} the minimal torque and T_x the torque at the time X. The moulded sheets were left one day at room temperature before commencing degradation and testing. The formulations used and their corresponding code are listed in Table 1.

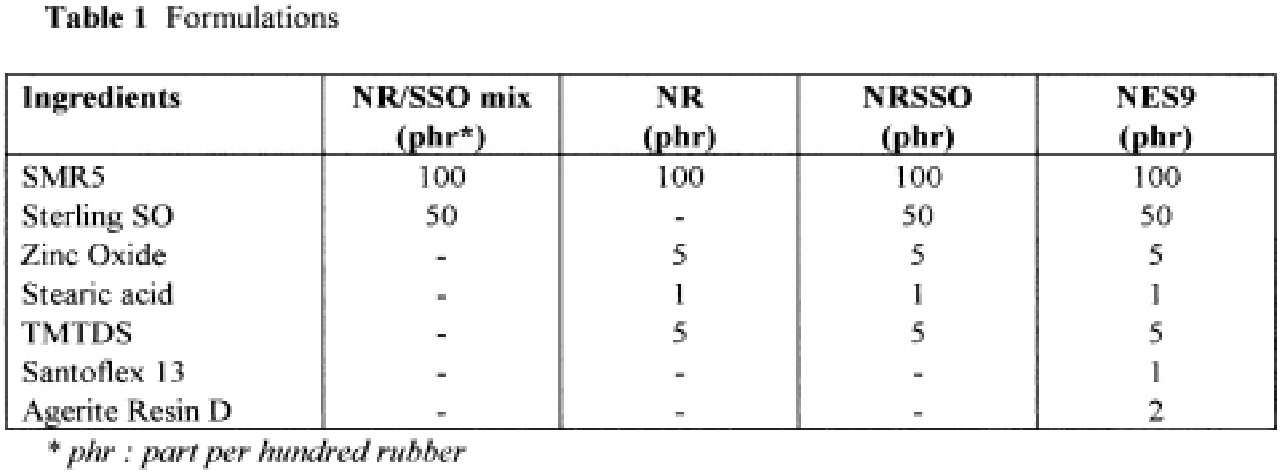


Table 1 Formulations

Ingredients	NR/SSO mix (phr*)	NR (phr)	NRSSO (phr)	NES9 (phr)
SMR5	100	100	100	100
Sterling SO	50	-	50	50
Zinc Oxide	-	5	5	5
Stearic acid	-	1	1	1
TMTDS	-	5	5	5
Santoflex 13	-	-	-	1
Agerite Resin D	-	-	-	2

** phr : part per hundred rubber*

Ageing procedure Samples were degraded for varying periods in air at 150 ± 1°C in a fan assisted laboratory oven. Five dumbbell shaped specimens (BS903 pt A2 type 2) were examined at each time interval and the samples were tested the day after removal from the ovens.

Mechanical properties Tensile testing was carried out to ASTM D-412, using a Hounsfield M Series tensometer fitted with a laser extensometer.

Swelling test The amount of toluene diffused into crosslinked rubber depends upon the number of crosslinks per unit volume of elastomer and/or the polymer-filler interactions. In order to assess the crosslink degradation of the elastomer network and/or destruction of polymer-filler interaction, the volume of toluene uptaken (V) per unit mass of sample was determined. Cured test pieces of dimensions 15 mm x 12 mm x 2 mm were accurately weighed. Each test piece was immersed in a glass vessel containing 30 cm^3 of toluene and left for 96h at room temperature in the dark. After immersion, the bulk of the toluene from the surface of the test pieces was removed with some filter paper, and the rubber samples were immediately weighed. This experiment was repeated three times and the median was taken.

Measure of dielectric loss of rubber samples This analysis was performed using a Marconi instrument 10 MHz-20 GHz Microwave Test Set 6200. A 20 mm x 4 mm x 2 mm rubber sample was cut along the mill direction and introduced vertically into a 75 mm x 10 mm x 10 mm glass tube (called empty cavity) located in the aperture of a specially made rectangular waveguide illustrated in Figure 1. The frequency range chosen for the analysis is 4.7-4.9 GHz which is a characteristic range for carbon black (Sterling SO) powder absorption. The microwave power loss at the resonant frequency of the rubber samples was determined relative to the empty cavity (dP in Figure 2) and normalised to the mass of the elastomer (dP/mass) and then plotted as a function of curing time at 150°C, and ageing time at a range of temperatures (130, 140 and 150°C). The error is estimated to ± 2% for power absorption.

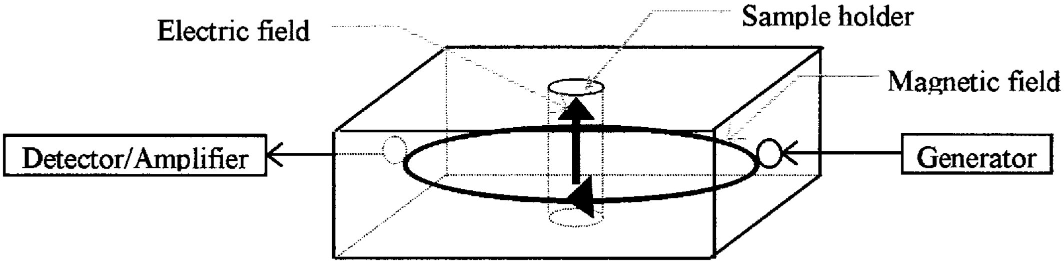


Figure 1 Diagram of the specially made rectangular waveguide.

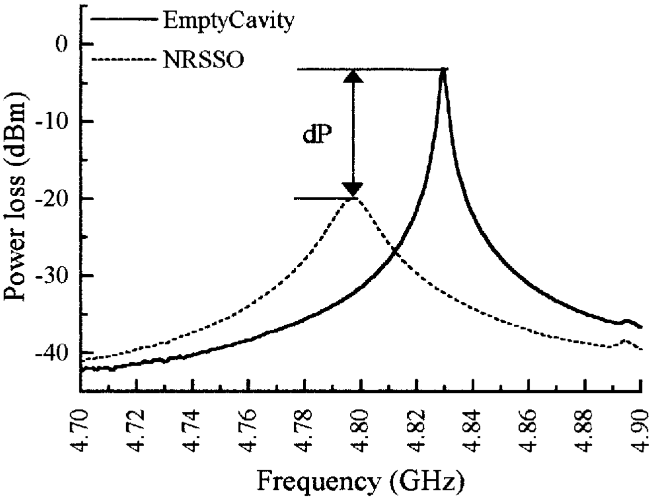


Figure 2 Microwave spectra obtained for filled natural rubber vulcanisate (NRSSO). dP is the power absorbed by NRSSO relative to the empty cavity absorption

Results and discussion

Thermo-oxidation of natural rubber was followed using microwave dielectric loss spectroscopy. The power absorbed per gram (dP/mass) of filled and unfilled natural rubber vulcanisate is plotted as a function of ageing time (Figure 3). In this figure a decrease in the power absorption as a function of ageing time at 150°C is observed only for the filled vulcanisate. This decrease is likely related to the destruction of filler-matrix interphase region during the thermo-oxidation.

It is significant that the reciprocal of volume swell as a function of ageing time follows an identical trend to dP/mass as a function of ageing time for the filled vulcanisate (Figures 4(b) and 6(a)). The same plot for the unfilled natural rubber vulcanisate is shown in Figure 4(a) and shows that there is no correlation between the microwave response and the reciprocal of the volume swell (1/V) as a function of time at 150°C. For the unfilled vulcanisate dP/mass remains constant (≈3 dBm/g) within the ageing period investigated. However there is a significant decrease in 1/V, and in this case, can be assigned to destruction of the crosslinks. This confirms that the variation of dielectric loss peak is associated exclusively with the filler-matrix interphase contribution to the network structure.

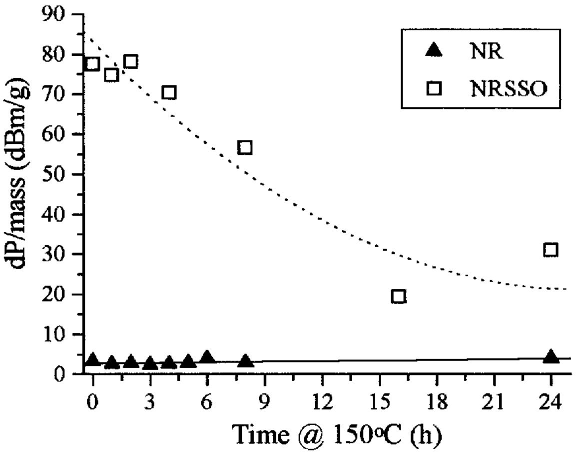


Figure 3 Power absorbed per gram as a function of ageing time at 150°C for filled and unfilled natural rubber.

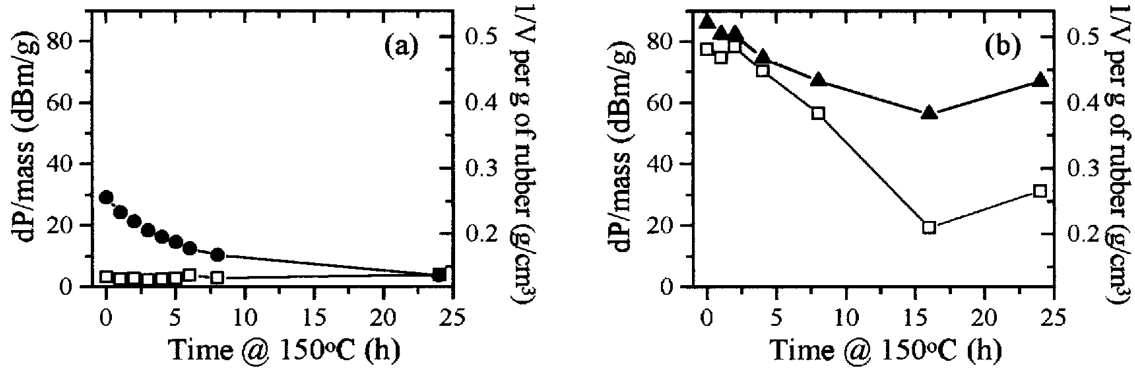


Figure 4 Correlation between microwave response (□) and the reciprocal of volume swell per gram of rubber (●) as a function of ageing time at 150°C for (a) the unfilled vulcanisate and (b) the filled vulcanisate.

dP/mass data for masticated natural rubber, uncured NR with curatives and NR cured for different times along with equivalent mixes containing Sterling SO have been studied. Table 2 indicates that, in the uncured state, curatives have no influence on the microwave response in both filled and unfilled formulations. However, addition of 50 phr of Sterling SO increases dP/mass from 1.9 to 9.3 dBm/g. This is probably due to interactions between rubber chains and carbon black particles that are formed during processing. Figure 5 shows that dP/mass is related to the degree of crosslinking in the case of NRSSO whereas no relationship is observed between power absorption and degree of cure for unfilled NR. It is likely that the curatives also promote formation of bonds between the natural rubber and the carbon black as well as between the rubber chains. This is reflected in the volume swell data which shows a reduction when 50phr of Sterling SO is added to the natural rubber.

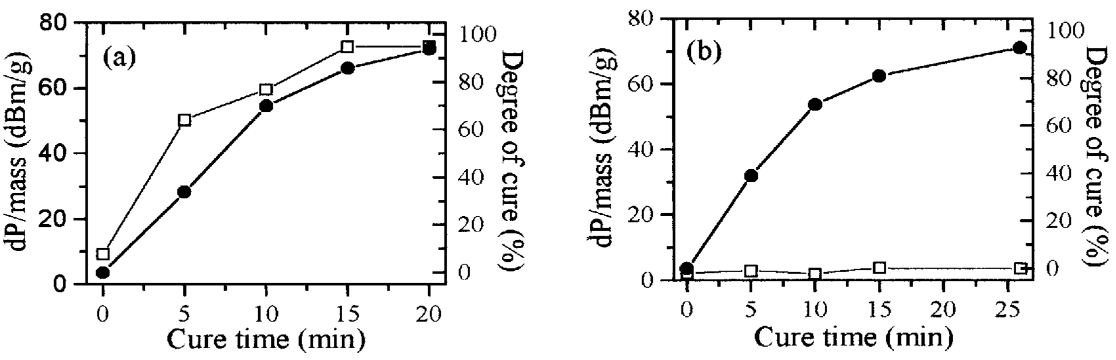


Figure 5 Correlation between microwave response (□) and degree of cure as a function of cure time (●) for (a) NRSSO and (b) NR.

Table 2

	Power absorbed/ g (dBm/g)	Level of cure (%)	Median of Volume of toluene uptaken (cm^3/g)
Masticate NR	1.89	-	-
Uncured NR (curatives)	2.17	0	∞
NR 5 min cured	2.82	39	4.94
NR 10 min cured	1.99	69	4.26
NR 15 min cured	3.84	81	4.03
NR 26 min cured	3.65	93	3.98
NR/SSO mix (no curative)	9.33	-	-
Uncured NRSSO (curatives)	9.29	0	-
NRSSO 5 min cured	50.25	34	2.38
NRSSO 10 min cured	59.61	70	2.22
NRSSO 15 min cured	72.61	86	2.17
NRSSO 20 min cured	72.64	94	2.05
NES9	36	93	2.27

The presence of hindered amine stabilisers in the filled vulcanisate was also studied at a slightly lower temperature of 140°C. The results obtained show that stabiliser addition causes a reduction in power absorbed for the unaged sample and an overall reduction in crosslink density compared to the NRSSO (Table 2). However the correlation between the swelling data and the microwave response is still evident (Figure 6(b)).

The increase in the power absorbed in the first hours of degradation shown in Figure 6(b) may be due to the displacement of stabiliser adsorbed on the carbon black by the rubber chains. After seven hours ageing at 140°C the dP/mass reaches a maximum and from this point the behaviour follows a similar trend, but at a lower rate of decrease, to the equivalent vulcanisate containing no stabiliser. The increase in the dP/mass observed towards the end of the ageing time, when the composite has only 10-20% of its initial tensile strength, may be associated with reformation of polymer-filler interactions via degraded matrix fragments which are likely to contain free radicals that are able to become attached to the carbon black surface.

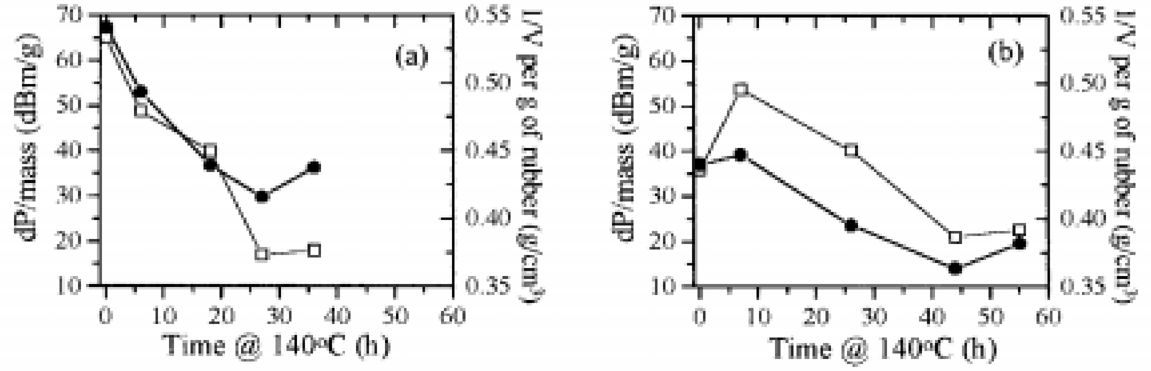


Figure 6 Correlation between microwave response (□) and the reciprocal of volume swell (●) as a function of ageing time (a) for filled natural rubber without antioxidant and (b) for filled natural rubber with hindered amine antioxidants.

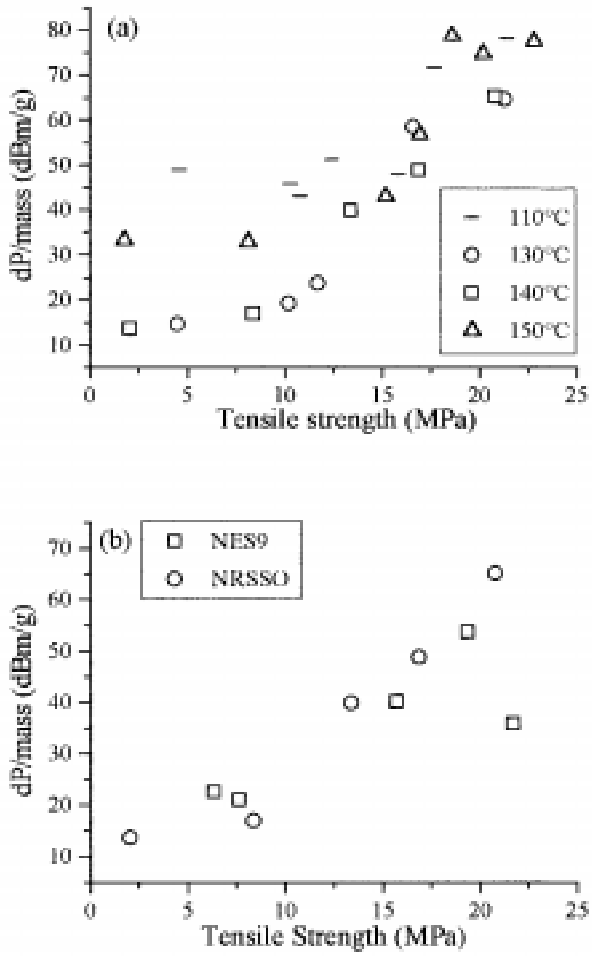


Figure 7 Relationship between the power adsorbed and the tensile strength (a) for filled natural rubber containing no antioxidant obtained for three different temperatures and (b) for filled natural rubber with (NES9) and without (NRSSO) antioxidants obtained at 140°C.

Retention of tensile strength, elongation to break and dP/mass as a function of ageing time show similar trends but are less marked than that observed for 1/V as a function of ageing time.

The filled natural rubber vulcanisate (NRSSO) was studied at different temperatures (110, 130, 140 and 150°C) and the relationship between the microwave response and the tensile strength was found to be exponential (Figure 7(a)).
Figure 7(b) shows that the presence of stabiliser in the formulation does not alter the exponential trend, however, the tensile strength (21.8 MPa) of the unaged composite containing stabiliser does not fit this relationship due to reason described above.

Conclusion

The changes in dP/mass in the microwave spectroscopy data can be attributed to carbon black-natural rubber interactions. Variations in the strength of these interactions due to thermal ageing can be followed using this technique. The effect of stabilisers on the microwave response has also been successfully demonstrated, and possible displacement of stabiliser adsorbed on the carbon black surface by the rubber chains can be observed, after which the composite behaviour follows a similar trend, albeit at a slower rate, to an equivalent unstabilised composite. Plotting tensile strength as a function of power loss for ageing carried out at a range of temperatures yields coincident data, which shows an exponential relationship and further highlights the specificity of the microwave technique to measurement of carbon black-natural rubber interactions. Other techniques such as solvent swelling measurements are only able to assess the combined effect of destruction of polymer-filler interactions and destruction of crosslinks within the bulk matrix.

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