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Effect of Rubber Chemicals on the Surface Free Energy of NR and NR–SBR Rubber Blends

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Rubber chemicals are added to raw rubbers to improve their mechanical, environmental and processing properties. These chemicals often migrate to the surface and alter its free energy and ultimately its contact adhesion properties. In this study, some industrially important rubber chemicals were mixed with natural rubber and a blend of natural rubber and styrene-butadiene rubber, and the contact angle measured using drops of water and diiodomethane on the rubber surface. The data from these measurements were subsequently used to calculate the surface free energy of the rubbers. Some of the chemicals had a detrimental effect on the surface free energy of the rubbers. This was also confirmed by static secondary ion mass spectrometry, which indicated a substantial surface modification of the rubbers.

Key words: rubbers; rubber chemicals; surface modification; secondary ion mass spectrometry; surface free energy; adhesion properties; NR-SBR rubber blends

Natural rubber (NR) has been with us for thousands of years. South American Indians used NR to make balls and to waterproof their clothes, bottles and shoes. In 1839, Charles Goodyear discovered that heating NR with sulphur, modified the rubber to retain its shape. As a result of this discovery, the rubber industry came into existence in 1846 by making solid rubber tyres for Queen Victoria's coaches. By 1855, the majority of the common rubber products we know today were invented[1].

The success of the rubber industry had been mainly due to its ability to improve the mechanical, physical and environmental properties of raw rubbers using a wide range of chemicals. These chemicals, to a large extent, control the properties of rubber vulcanisates or cured rubbers[2], and enhance the durability, performance and service life of rubber products such as tyres, conveyor belts, hoses, and seals. At least eight classes of rubber chemicals namely; curing agents, accelerators, activators, fillers, processing aids, antidegradants, colour pigments and flame retardants are present. Curing agents such as sulphur when used in combination with accelerators and activators at elevated temperatures, *i.e.* 140ºC – 240ºC, form thermally stable cova-

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lent bonds between the rubber at the carbon-carbon double bonds which are present in unsaturated rubbers, *e.g.* NR. Colloidal carbon black fillers improve the mechanical properties of rubber vulcanisates for example tear strength, abrasion resistance and hardness. Other processing aids reduce the rubber viscosity and make it easier to shape the rubber. Antidegradants protect the rubber against environmental ageing. Colour pigments alter the colour of white filled rubbers, and flame retardants prevent rubber from burning easily. Some studies have shown that antiozonants (antidegradant) migrate to the surface of NR and alter its composition[3]. Importantly, when dissimilar rubbers are blended together, it is essential that strong interfacial adhesion is formed between them. Understanding the effect of rubber chemicals on the surface free energy and contact adhesion of rubbers is of significant importance to the users of these rubber blends[4,5].

For example, in one study, Ansarifar and co-workers[5] examined the effect of high abrasion furnace and medium thermal carbon blacks on the self-adhesion of NR as a function of contact time by means of peel tests. Peel energies were measured for a peel angle of 180º in ambient temperature at a constant rate. The self-adhesion of the raw unfilled NR reached its maximum value before the first contact time investigated (~3 min), and the locus of failure deviated randomly away from the interface into the bulk of the rubber. The addition of high abrasion furnace black to the NR reduced the adhesion level and there was no sign of an increase of the adhesion with time. Moreover, the failure locus followed the interface in all the tests. Surprisingly, the self-adhesion of NR filled with the same amount of thermal black showed a different behaviour from the high abrasion furnace black filled rubber. The plateau adhesion was increased further, and the adhesion rose during the first 20 h of contact. The results showed that the presence of the medium thermal black in NR did not prevent the development of strong levels of self-adhesion. Indeed, the addition of the black raised the level of adhesion attainable after long contact times. It was concluded that the influence of carbon black on the self-adhesion of NR depended strongly upon the type of black.

Contact angle measurement has been used extensively to study the surface modification of NR. Sruanganurak and co-workers[6] deposited poly(methyl methacrylate) particles onto an NR latex film surface and confirmed an increase in hydrophilicity of the surface. The measurement was also sensitive to surface oxidation, which caused a significant reduction in the film's contact angle. The surface modification of NR latex films by argon plasma treatment, as well as by UV-induced graft copolymerisation of the plasma-pretreated films were found by other workers to impart new surface properties such as hydrophilicity or hydrophobicity[7]. These measurements also revealed that the hydrophilicity of the NR surface was considerably enhanced by both treatments. These studies and many others[8–11] have shown that the contact angle measurement was a suitable technique for assessing the effects of different pre-treatments on the surface free energy (SFE) of rubbers. However, there is comparatively limited information on the effect of the migration of rubber chemicals to the surface of NR, and its subsequent influence on the free energy of the NR surface remains relatively unknown.

The aim of this study was to assess the effect of a wide range of industrial rubber chemicals on the surface free energy of NR and a blend of the NR with styrene-butadiene rubber using contact angle measurement. Static secondary ion mass spectrometry was also employed to determine surface compositional modification of the rubber in the presence of the chemicals.

EXPERIMENTAL

Materials

The raw elastomers used were standard Vietnam natural rubber grade SVR CV60 (constant viscosity 60) and styrene-butadiene rubber (SBR) (Intol 1500®, Enichem) with a viscosity of 52 Mooney units[12]. Both rubbers were non-polar hydrocarbon polymers. The reinforcing fillers were high abrasion furnace (HAF) (N330), general purpose furnace (GPF) (N660) and medium thermal (MT) (N990) carbon blacks. Full details of the composition and particle size of these fillers are given in *Table 1*.

In addition to the raw elastomer and fillers, the other additives were tetramethyl-thiuramdisulphide (TMTD) (accelerator), 2-morpholinobenzothiazole (MBS) (accelerator), stearic acid (activator), zinc oxide (activator), oil coated sulphur (curing agent), N-(1,3-dimethylbutyl)-N′-phenyl-*p*-phenylenediamine (Santoflex 13) (antioxidant) (6PPD), N,N′-diaryl-*p*-phenylenediamine (antioxidant) (DTPD), and aromatic oil and paraffin wax (processing aids). In total, fourteen compounds (Compounds 1 and 2 being raw SBR and NR) were prepared for this study (*Table 2*). In addition to these compounds, a fully formulated blend of the NR and SBR rubbers containing 90 p.h.r. NR, 10 p.h.r. SBR, 31 p.h.r. high abrasion furnace black, 6 p.h.r. aromatic oil, 4 p.h.r. zinc oxide, 1 p.h.r. stearic acid, 2 p.h.r. paraffin wax, 2 p.h.r. Santoflex 13, 1 p.h.r. dihydroquinolines (antioxidant metal inhibitor) (TMQ), 1.2 p.h.r. N-*t*-butyl-2-benzothiazolesulphenamide (TBBS), 0.19 p.h.r. TMTD (80% active) and 2 p.h.r. oil coated sulphur was also included in this study. This compound was mixed in two stages at Avon VMS, UK, and had a total mixing time of 680 seconds. Its viscosity was 37 Mooney units[12], and it had a glass transition temperature of –65ºC. This was referred to as Compound 15 in *Table 3*.

Mixing

Compounds 3-14 (*Table 2*) were prepared in a Haake Rheocord 90, a small-size laboratory mixer with counter rotating Banbury rotors. The mixing chamber was thoroughly cleaned with toluene every time a rubber compound was prepared and a mixing cycle of 5 min was used for preparing the rubbers. Before mixing started, the temperature of the mixing chamber was 65ºC. The rotors were started at 50 r.p.m. and the raw rubber together with the chemical additives were mixed until the rubber compound reached 70ºC. The rotor speed was subsequently reduced to 33 r.p.m. until mixing was over. The volume of the mixing chamber was 78 cm^3, and a fill factor of 0.43 was used for preparing the compounds. Haake Software Version 1.9.1. was used for controlling the mixing conditions and storing data.

TABLE 1. COMPOSITION (% BY MASS) AND AVERAGE PARTICLE SIZE OF CARBON BLACKS USED IN THE PRESENT STUDY

Carbon black	Carbon %	Hydrogen %	Oxygen %	Sulphur %	Ash %	Mean particle diameter[a] (nm)
HAF	97.96	0.30	0.83	0.59	0.32	32
GPF	98.64	0.36	0.22	0.55	0.23	70
MT	99.42	0.33	0.00	0.01	0.27	300

[a]surface mean averages from electron microscopy.

TABLE 2. RECIPE FOR THE RUBBER COMPOUNDS TESTED

Formulation (p.h.r.)[a]	Compound number													
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
SBR (Intol 1500)	100	–	–	–	–	–	–	–	–	–	–	–	–	–
SVR CV60	–	100	100	100	100	100	100	100	100	100	100	100	100	100
N330	–	–	30	–	–	–	–	–	–	–	–	–	–	–
N660	–	–	–	17.5	–	–	–	–	–	–	–	–	–	–
N990	–	–	–	–	33	–	–	–	–	–	–	–	–	–
TMTD	–	–	–	–	–	0.49	–	–	–	–	–	–	–	–
MBS	–	–	–	–	–	–	0.72	–	–	–	–	–	–	–
Stearic acid	–	–	–	–	–	–	–	1	–	–	–	–	–	–
Zinc oxide	–	–	–	–	–	–	–	–	4	–	–	–	–	–
Oil coated sulphur	–	–	–	–	–	–	–	–	–	1.75	–	–	–	–
6PPD	–	–	–	–	–	–	–	–	–	–	2	–	–	–
DTPD	–	–	–	–	–	–	–	–	–	–	–	1.5	–	–
Aromatic oil	–	–	–	–	–	–	–	–	–	–	–	–	2	–
Paraffin wax	–	–	–	–	–	–	–	–	–	–	–	–	–	2

[a] p.h.r.: parts per hundred by weight

TABLE 3. RESULTS FROM THE CONTACT ANGLE MEASUREMENTS AND THE SURFACE FREE ENERGIES OF THE 15 COMPOUNDS TESTED

Compound number	$\theta_{diiodomethane}$	θ_{water}	γ_s^d (mN/m)	γ_s^p (mN/m)	γ_s (mN/m)
1	59.5±7.1	90.1±3.4	28.9	2.4	31.3
2	71.1±5.8	89.4±3.0	22.3	4.3	26.5
3	63.8±2.1	97.3±1.6	1.2	26.4	27.6
4	64.9±3.5	92.4±3.5	2.4	25.8	28.2
5	66.7±3.7	92.8±3.0	2.5	24.8	27.3
6	86.6±2.6	97.4±1.6	3.9	14.3	18.2
7	84.8±3.2	99.2±2.1	3.1	15.1	18.1
8	89.4±3.4	107.9±2.0	1.4	13.0	14.4
9[a]	–	–	–	–	–
10	73.9±3.6	95.4±2.8	2.7	20.7	23.4
11	80.0±3.8	91.8±2.3	4.7	17.5	22.2
12	80.1±3.4	96.2±1.3	3.3	17.4	20.7
13	74.9±2.5	95.4±2.1	2.8	20.2	23.0
14	88.2±3.4	111.7±3.0	0.7	13.5	14.2
15[b]	82.5±2.7	114.2±1.7	16.3	0.14	16.4
15[c]	79.5±3.0	107.1±1.3	17.8	0.7	18.5

[a] No reliable measurements could be made for compound 9 as the contact angle changed significantly from one drop to another.

[b] Uncured NR and SBR blend. Formulation: 90 p.h.r. NR, 10 p.h.r. SBR, 31 p.h.r. HAF, 6 p.h.r. aromatic oil, 4 p.h.r. zinc oxide, 1 p.h.r. steraic acid, 2 p.h.r. paraffin wax, 2 p.h.r. Santoflex 13, 1 p.h.r. dihydroquinolines (antioxidant metal inhibitor) (TMQ), 1.2 p.h.r. TBBS, 0.19 p.h.r. TMTD (80% active), and 2 p.h.r. oil coated sulphur.

[c] Cured NR and SBR blend. Compound 15 was mixed at Avon VMS, UK.

Test Procedure and Test Pieces

After the rubber compounds were prepared, they were placed in a mould, 8 cm by 8 cm in dimension to produce 1 mm thick rubber sheets. Poly ethylene terephthalate (PET) film was used to prevent the mould surfaces from contaminating the rubber. Note that the PET used was a food grade polyester film with an ultra-low additive content. Such a film provided a release layer without introducing contamination to the rubber surfaces.

Extensive testing using contact angle analysis showed no evidence of contamination or transfer of material either from the rubber onto the PET surface or from the PET onto the rubber. When the rubber was placed in the mould, it was kept at 150ºC for 5 min to soften and then for an extra 20 min at the same temperature under a pressure of 1.3 MPa to produce smooth sheets. The mould was subsequently removed and allowed to cool down at ambient temperature under the same pressure. Twenty minutes after the rubber sheets were prepared, samples measuring approximately 60 mm by 25 mm, were cut from the sheets and one side of the rubber was secured onto a flat glass plate using double sided adhesive tape. The PET film was removed from the top surface and the sample was immediately presented for contact angle analysis. It was envisaged that a secondary role of the PET film was to provide a reasonably uniform surface topography for all filled polymers. This was to obviate the problems associated with the measurement of contact angles on surfaces of different texture.

Measurement of the Glass Transition Temperature of the Rubbers

The glass transition temperature of the rubbers was determined using a TA Instrument 2920 Modulated temperature (M-TDSC) calorimeter. Measurements under nitrogen were conducted from –120ºC to 20ºC at a heating rate of 3ºC/min. The oscillation amplitude was ±1.5ºC for a period of 60 s.

Procedure for Measuring the Contact Angle of the Rubber Surfaces

The fluids used were triple distilled water (polar) and diiodomethane (non-polar). At least 10 drops were placed on each rubber surface using a computer controlled dispensing unit in a Contact Angle System OCA 20 (Data Physics Instruments) at 20ºC and 20% relative humidity. The OCA 20 software was used to control the volume of the liquid drop, typically 2 microlitres, dispensed at a rate of 1 microlitre per second. The software was also used to collect, store and process the contact angle data, θ_{water} and $\theta_{diiodomethane}$ (*Table 3*) to calculate the dispersive and polar components of the surface free energy. In this study we used the recently advanced contact angle method measuring both sides of the droplet and using the average value for calculation of the surface free energies. Note that no significant asymmetry was observed from the drop shape on any surface and that the contact angles did not change with time as this could have indicated contamination of the test liquids. In addition, a study was undertaken to deliberately roughen rubber surfaces prior to contact angle measurement. This preliminary study showed that the degree of roughness introduced using the sample preparation method described in the test procedure did not influence the contact angle values. The authors cannot exclude the possibility of the rubber and rubber blends providing heterogeneous surfaces on a nanometre or micrometre scale. It is recognised that the contact angle procedure used provides a macroscopic view of these surfaces rather than providing details of different phases present in the plane of the surface.

Static Secondary Ion Mass Spectroscopy (SSIMS) of the Rubber Samples

The instrument used was a Cameca 3F operating with O_2^- primary ions with 15keV energy and a fluence below the static threshold. This meant that ion current density was very low so that only the outer atomic layer was ionised and analysed. The analyser used was a magnetic sector type giving a mass resolution (m/Δm) of greater than 300, where m represents mass, and Δm, change in mass. The samples analysed were either unfilled NR, sample 2 in *Table 2*, SBR or various additives which had undergone the same thermal cycle as the cured rubber. Prior to this thermal cycling, the additives were either dried onto aluminium foil or embedded into indium foil to facilitate analysis.

RESULTS AND DISCUSSION

Effect of Rubber Chemicals on the Surface Free Energy of NR and a Blend of NR and SBR by Contact Angle Measurement

Table 3 summarises the surface free energies of the rubbers containing different rubber chemicals calculated from the contact angles. The raw NR had a surface energy of about 27 mN/m (mili Newton/metre). Evidently, the chemicals influenced the surface energy of the rubber in different ways. For example, stearic acid and paraffin wax were detrimental and reduced the surface energy to about 14 mN/m. When TMTD and MBS were added, the surface energy decreased to about 18 mN/m and with DTPD, a value of 21 mN/m was obtained. Interestingly, when similar rubber chemicals, including paraffin wax, were mixed with a blend of the NR and SBR, the surface free energy decreased to about 16 mN/m (Compound 15) (*Table 3*). This was noticeably lower than the free energies of the raw SBR and NR (Compounds 1 and 2, respectively), which were close to 31 mN/m and 27 mN/m, respectively. Clearly, the addition of the chemicals had a detrimental effect on the surface free energy of the rubber blend. Considering the contact angle data in *Table 3*, it was evident that the lower values of the surface energy were of significant importance. It is also noteworthy that the surface free energy of Compound 15 remained almost at the same level, *i.e*.18.5 mN/m, when it was fully cured at 150ºC for 7 min. This indicated that the surface free energy of the filled blend was unaffected by the reaction of the curing agents and formation of crosslinks in the rubber. Note that extensive testing was carried out to study the influence of the PET release strip in terms of contamination or introduction of roughness onto the moulded surfaces. It was not believed that these were significant factors on the results reported in *Table 3*. Note that no reliable contact angle could be determined from the zinc oxide powder. This is most likely to be a function of the surface porosity of the powders used. It is also noted that metal oxides are generally regarded as high energy surfaces.

The surface free energies of the NR filled with high abrasion furnace and medium thermal blacks were 27 mN/m, and were similar to the unfilled rubber (*Table 3*). The addition of these fillers did not alter the surface energy of the NR. However, in spite of this, the self-adhesion of the black filled NR was affected by the type of the filler[5].

In peel tests, the work required to separate a unit area of the surface provides an indirect measure of the strength of adhesion. One mechanism which can use up part of the work done is irreversible deformation associated with the peel bend[13]. Plastic yielding and hysteresis can cause energy losses in the peel bend[14–18]. Materials such as NR show high degree of hysteresis, and therefore, they suffer from significant viscoelastic losses as

the rubber adherent passes through the peel bend[19]. The effect of carbon black fillers including high abrasion furnace and medium thermal on the viscoelastic behaviour of NR was studied[20]. It emerged that the type of filler influenced the energy losses in the rubber and was responsible for the different self-adhesion energies of the black-filled rubbers.

Apparently, there was no correlation between the surface free energy of the NR filled with abrasion furnace and medium thermal carbon black fillers in the present investigation and the self-adhesion energy measured for the rubber in a previous study[5]. The viscoelastic energy losses in the bulk of the rubber were responsible for the latter, whereas the former was purely a surface energetic phenomenon.

Secondary Ion Mass Spectrometry of the Rubber Samples

The aim of the SSIMS was to provide molecular fingerprint information in order to positively identify compounding chemical components which underwent surface migration. From the contact angle analysis, a number of candidate materials were identified which were most likely to be responsible for the low observed SFE on fully compounded NR-SBR rubbers as a consequence of their surface migration, these were, stearic acid, paraffin wax, TMTD, MBS and zinc oxide. In addition, unmodified NR and SBR and both uncured and fully cured compounded NR–SBR were analysed by SSIMS for control purposes. *Figures 1a* to *1i* show representative SSIMS spectra up to approximately 300 atomic mass units (amu). *Figure 1a* from the unmodified NR gives major peaks at 27, 41, 43, 55, 57, 67, 69, 73 and 81 atomic mass units. In contrast, the SBR had peaks at 27, 29, 41, 43, 59, 67, 77, 79 and 91 amu (*Figure 1b*). The presence of major peaks at 59 and 91 amu in the SBR spectra and the absence of a large peak at 43 amu were amongst the ways of discriminating between the NR and SBR.

The fully formulated, filled, uncured NR-SBR blend, Compound 15*, produced entirely different spectra compared with either NR or SBR controls with more significant peaks at 57, 69, 71, 83 and 97 amu and a less apparent peak at 41 amu than observed in either unfilled rubber (*Figure 1c*). The cured blended rubber, Compound 15** in *Table 3*, gave very similar spectra to the uncured (*Figure 1d*). Unlike either the cured or uncured, filled blend, the stearic acid gives relatively small signals at 57, 69 and 81 amu (*Figure 1e*). Similarly, the lack of peaks at 71 and 97 amu and the presence of a peak at 147 amu means that TMTD can also be excluded as a surface migrating species (*Figure 1f*). MBS gives one major peak at 88 amu which is absent on both uncured and cured blended NR-SBR surfaces (*Figure 1g*). Similarly, major peaks at 88, 101, 167 and 207 in *Figure 1h*, provided by the zinc oxide control indicate that this material is not predominantly on the surface of the processed NR-SBR blend. In contrast, there is very good agreement with the spectra from the paraffin wax (*Figure 1i*). Comparing *Figures 1c*, *1d* and *1i*, it can be seen that all of the major peaks are present in roughly the same peak ratios.

In summary, the surface of the filled NR-SBR polymer blend is in fact, dissimilar in composition to both NR and SBR constituents. This is the case for both uncured and cured material indicating that some surface migration has occurred by one or more rubber chemicals within the additive package. Although SSIMS is not generally regarded as a quantitative technique, the good agreement between the spectra from heat cycled paraffin wax and the surface of the filled NR-SBR strongly suggests that this is the dominant migrating species under the thermal cycling conditions used.

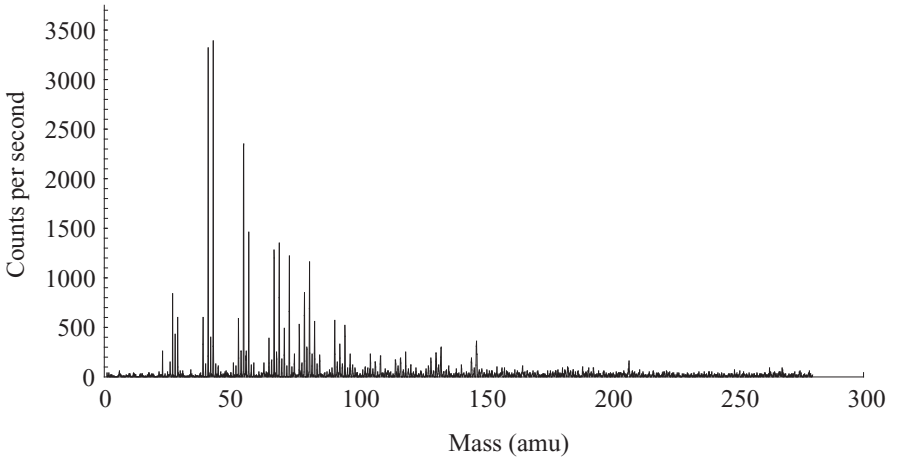

Figure 1a. SSIMS scan, 0 – 300 amu, from an unfilled NR sample (Compound 2).

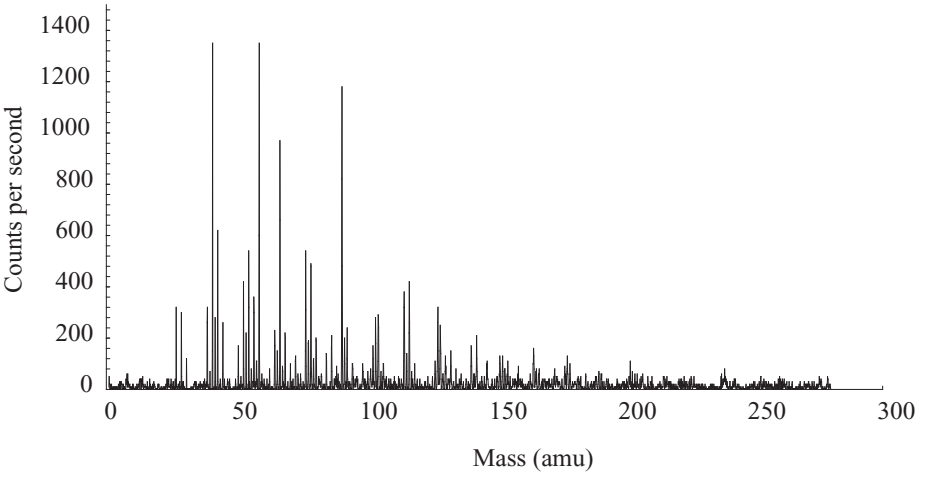

Figure 1b. SSIMS scan, 0 – 300 amu, from an unfilled SBR sample (Compound 1).

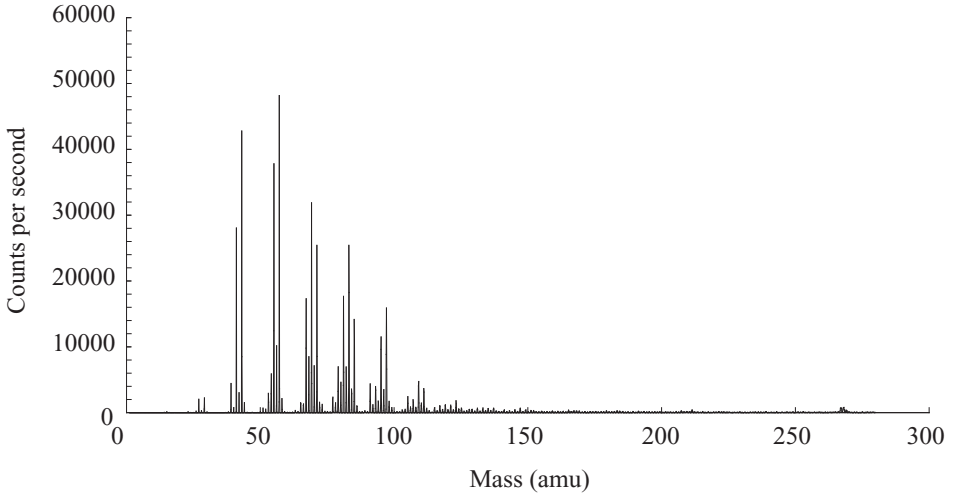

Figure 1c. SSIMS scan, 0 – 300 amu, from an uncured, filled NR-SBR sample (Compound 15).*

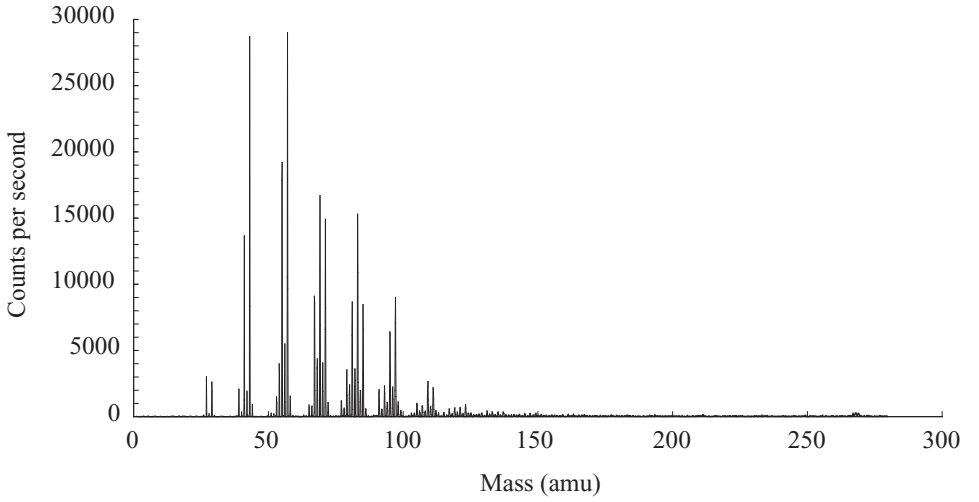

*Figure 1d. SSIMS scan, 0 – 300 amu, from a cured, filled NR-SBR sample (Compound 15**).*

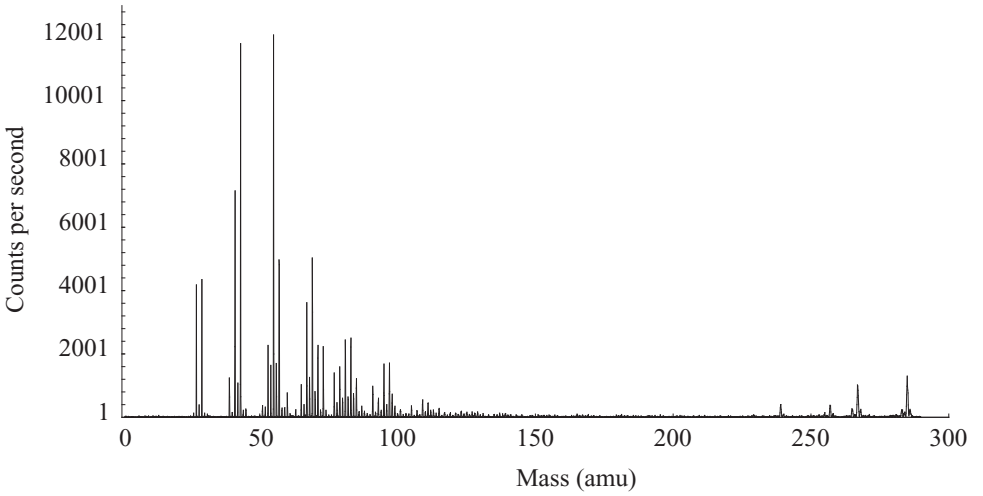

Figure 1e. SSIMS scan, 0 – 300 amu, from a heated stearic acid sample.

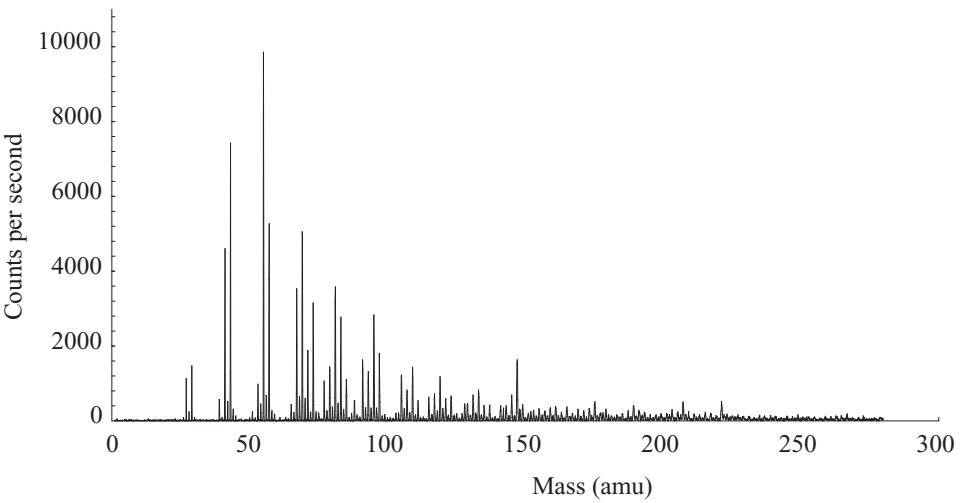

Figure 1f. SSIMS scan, 0 – 300 amu, from a heated TMTD sample.

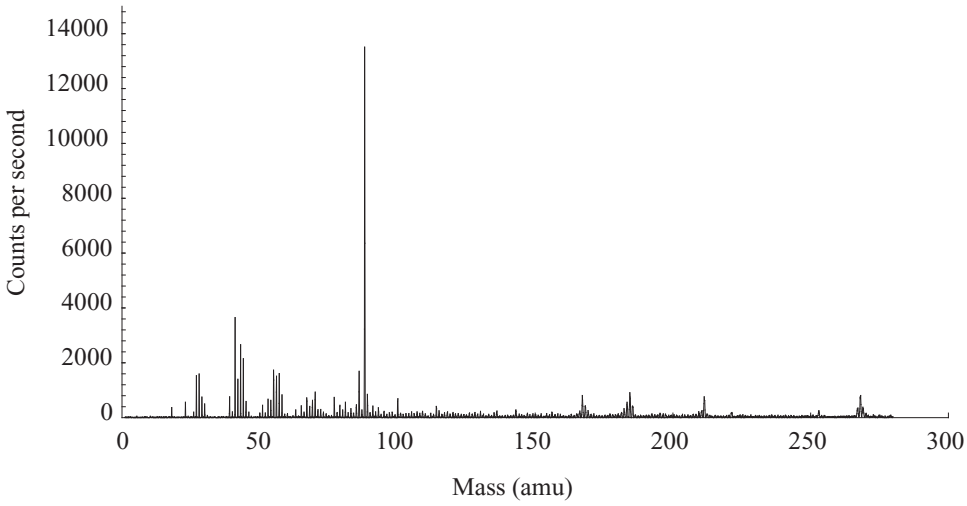

Figure 1g. SSIMS scan, 0 – 300 amu, from a heated MBS sample.

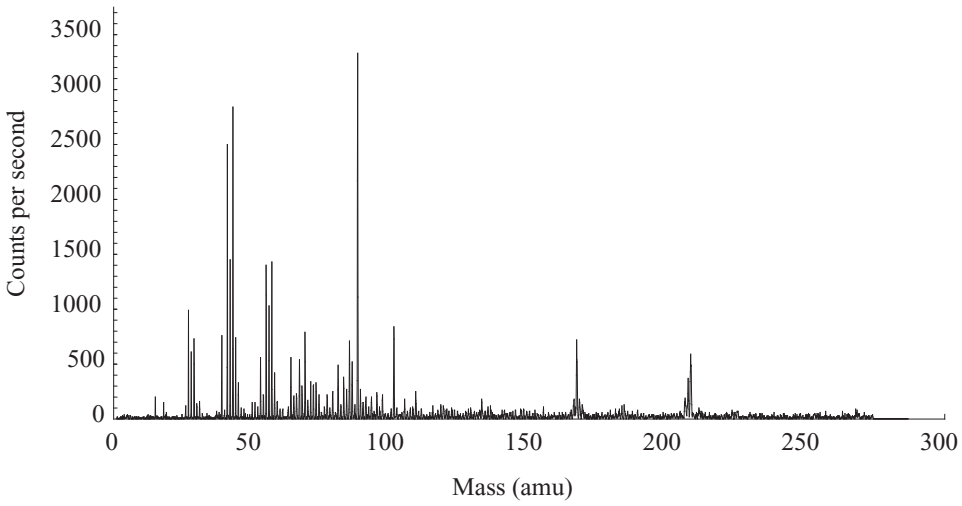

Figure 1h. SSIMS scan, 0 – 300 amu, from a heated zinc oxide sample.

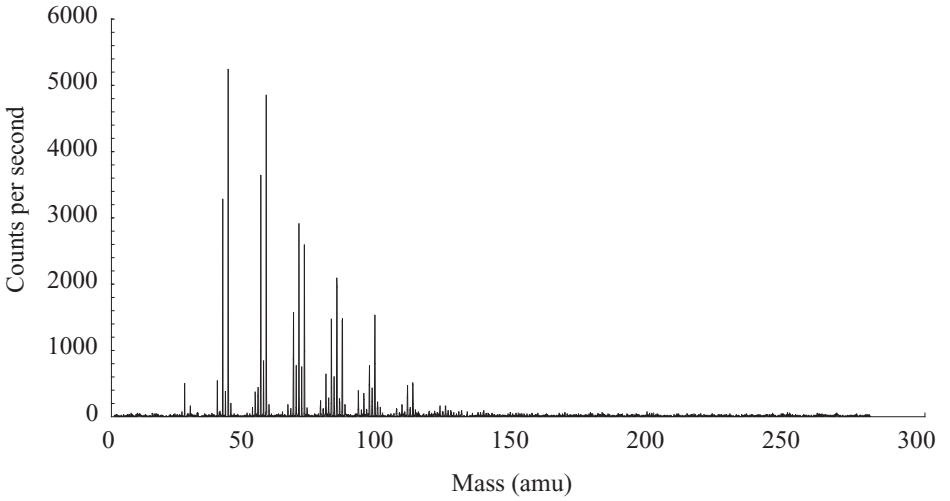

Figure 1i. SSIMS scan, 0 – 300 amu, from a heated paraffin wax sample.

CONCLUSIONS

This study has shown that adding different rubber chemicals to natural rubber had significantly altered the surface free energy and chemical composition of the modified rubber. In particular, it can be concluded that:

- The addition of paraffin wax and stearic acid had the largest effect on the surface free energy of the NR, reducing it by about 45%. TMTD and MBS were also detrimental though to a lesser extent, reducing the surface free energy of the rubber by approximately 30%. A similar feature was also observed when the chemicals were mixed with a blend of the NR and SBR and then tested by the contact angle measurement.

- Static secondary ion mass spectroscopy directly observed the migration of paraffin wax to the surface of both the NR and the NR-SBR blends. The large reduction in surface free energy was attributed to this migration. The remaining chemicals had a relatively minor effect on the surface composition of the NR.

- In addition, and in the light of previous studies, it should be noted that there is the absence of a correlation between the self-adhesion energy measured in a previous study[5] and surface free energy of the NR filled with abrasion furnace and medium thermal black fillers in the present investigation. The early indications were that the surface free energy measurements could not be used to predict the development and strength of the self-adhesion of the NR.

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