



## PHYSICOCHEMICAL CHARACTERISTICS OF RECYCLED TYRE TREAD COMPOUNDS

(Ciri-Ciri Fizik-kimia Sebatian bagi Bunga Tayar Kitar Semula)

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### Abstract

The present work was aimed at evaluating the physicochemical characteristics of seven recycled tyre tread compounds. The materials were characterized for elemental composition, surface morphology, surface chemistry, oil content, ash content, thermal degradation and dielectric properties. Some of the materials were analyzed according to the Rubber Research Institute Malaysia (RRIM) in-house methods for comparison. Natural rubber, butadiene rubber and styrene-butadiene rubber were also employed to validate the thermal degradation profile. Results show that all materials exhibit comparable elemental composition, and dielectric and surface properties, but dissimilar composition of rubber compounds as revealed by the simple mass balance-thermogravimetric approach. The finding is consistent with the RRIM in-house methods. The proposed thermogravimetric approach is sufficient to assess the composition and quality of recycled tyre tread compounds.

**Keywords:** recycled tyre tread compound, physicochemical characteristic, mass balance-thermogravimetric approach

### Abstrak

Kajian ini bertujuan untuk menilai ciri-ciri fizik-kimia tujuh sebatian bagi bunga tayar kitar semula. Bahan-bahan tersebut dicirikan berdasarkan komposisi unsur, morfologi permukaan, kimia permukaan, kandungan minyak, kandungan abu, kemerosotan terma dan sifat dielektrik. Beberapa bahan telah dianalisis mengikut kaedah dalaman Institut Penyelidikan Getah Malaysia (RRIM) untuk perbandingan. Getah semulajadi, getah butadiena dan getah stirena-butadiena juga digunakan untuk mengesahkan profil kemerosotan terma. Keputusan menunjukkan bahawa semua bahan mempamerkan komposisi elemen, dan sifat dielektrik dan permukaan yang hampir serupa, tetapi komposisi sebatian getah yang berbeza seperti didedahkan oleh pendekatan mudah termogravimetrik-imbangan jisim. Penemuan ini sejajar dengan kaedah dalaman RRIM. Pendekatan termogravimetrik yang dicadangkan ini memadai untuk menilai komposisi dan kualiti sebatian bagi bunga tayar kitar semula.

**Kata kunci:** sebatian bagi bunga tayar kitar semula, ciri fizik-kimia, pendekatan termogravimetrik-imbangan jisim

### Introduction

There is an increasing concern over the quality of incoming recycled material for the manufacturing of tyre tread compounds. Often, the recycled material is a blend of different tyre segments [1]. The parts and segments of tyre generally contain varying composition of rubber constituents. Because of the similar physical appearance, the source and composition of this material are somewhat complicated to be differentiated, hence compromising the quality of the tyre treads produced.

In the manufacturing of tyre treads especially for heavy vehicles such as buses and trucks, the recycled material of sufficient quality should be used. The tread is normally composed of natural rubber and poly-butadiene rubber with the right proportion, as these two constituents offer high resistance to abrasion, resistance to cracking and low heat build-up [2]. Failure to attain the correct rubber composition would definitely lead to the inferior quality of tyre tread that may as well compromise the tyre safety. In the present practice, the readily formed tyre tread compound of unknown composition is tested for physicochemical and mechanical characteristics to ascertain its quality and suitability for heavy vehicles [3]. This trial-and-error approach is time-consuming and expensive, and commonly leads to unsatisfactorily outcomes. Consequently, the compound may end-up be rejected because of the quality and safety issues [3].

It is imperative to understand the nature and composition of the recycled materials beforehand. Therefore, the present work is aimed at evaluating the physicochemical characteristics of seven generic recycled materials of tyre treads to shed some light on fast and reliable quality estimation. The compounds were characterized for elemental composition, surface morphology, surface chemistry, oil content, ash content, thermal degradation and dielectric properties. A simple mass balance-thermogravimetric approach was proposed to ease the estimation of rubber constituents in these compounds. The results were compared and validated with the in-house method of Rubber Research Institute of Malaysia (RRIM).

### Materials and Methods

Seven generic recycled materials to produce tyre tread compounds from anonymous sources, natural rubber (NR), butadiene rubber (BR), styrene-butadiene rubber (SBR) and Tube-X were supplied by Revocomm Technologies Sdn Bhd. The seven generic samples of unknown composition and quality were designated as SP40-X, SR-X, AP40, EcP40, Sh9(2), Sh8(2) and Sh-PT. A numeral 40 indicates 40-mesh recycled materials. Hexane was supplied by QReC (Malaysia), and is of analytical-grade reagent.

The materials were analyzed for elemental composition (CHNOS) using a VarioMICRO elemental. The surface functional groups were determined using a FTIR spectrometer (Perkin Elmer, Spectrum One). The thermal degradation profiles were obtained using a TGA equipment (Perkin Elmer, TGA 7) under N<sub>2</sub> flow with a heating rate of 10 °C/min. A FESEM-EDX (Hitachi, SU8020) was used to evaluate the surface morphology of materials. The dielectric properties of materials were determined using a vector network analyzer (Agilent, HP8720B) at varying frequencies. Some the compounds, namely SP40-X, AP40, EcP40 and Sh9(2) were tested by an in-house method of Rubber Research Institute of Malaysia (RRIM) for comparison and validation.

The materials were subjected to heating in a furnace at 850 °C for 2 hours. The residue, namely ash content was calculated as the residual mass over the original mass before heating. The oil extraction was performed by refluxing hexane using a Soxhlet apparatus. The solvent was recovered using a rotary evaporator and the oil content was calculated as the mass of oil over the mass of solid compound before extraction.

### Results and Discussion

Table 1 shows the elemental composition and ash content of recycled tyre tread compounds. The ash content varies between 3.7% and 8.2%. Nevertheless, the composition of ash (carbon black or silica, and zinc oxide) and sulphur are still within the range allowed for truck tyre treads, i.e., 2.0% - 22% and 1.0% - 2.5%, respectively [1, 4]. Because the rubber materials are purely hydrocarbon, the presence of oxygen in the compounds could be attributed to the use of ZnO as filler. SP40-X exhibits a higher ash content, while SR-X shows a 2.2 times lower ash content than SP40-X. The finding suggests that, although these two materials are from the same anonymous source, their blended composition and the quality of compound produced are not uniform.

Table 1. Elemental composition and ash content

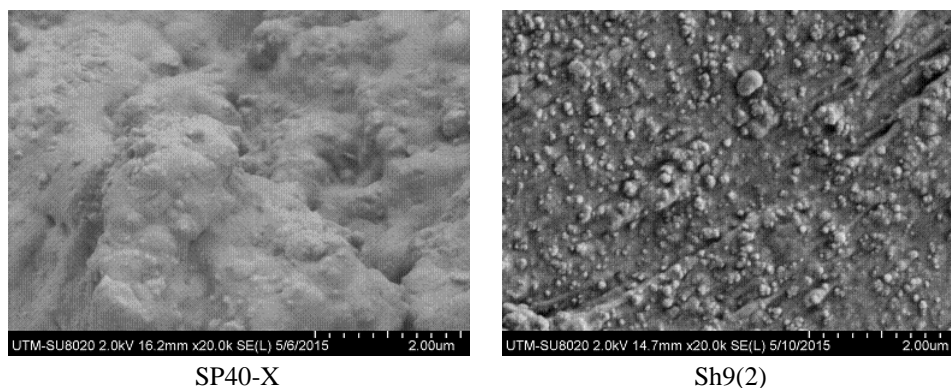
Generic ID	Ash Content (%)	Elemental Composition (%)				
		Carbon	Hydrogen	Nitrogen	Sulphur	Oxygen*
SP40-X	8.15	81.3	7.31	0.52	2.23	0.49
SR-X	3.67	83.8	7.40	0.33	1.67	3.13
AP40	6.93	81.5	7.48	0.48	2.07	1.54
EcP40	6.19	83.3	7.40	0.33	1.78	1.00
SH9(2)	5.09	82.1	7.74	0.43	2.19	2.45
SH8(2)	5.17	82.5	7.72	0.42	2.27	1.92
Sh-PT	5.02	82.4	7.68	0.43	2.10	2.37

\*Calculated by difference

All ash samples show a common silver colour that probably indicates the presence of inorganic Zn metal (ZnO). In addition, the ash samples of AP40 and Sh-PT are slightly brownish. SP40-X and SR-X exhibit a trace carbon residue that remains even after the heating process. The finding implies that SP40-X and SR-X could contain some fraction of fixed carbon (probably carbon black powder) that can withstand a longer heating period at a higher temperature. Further, it should be noted that carbon black powder is rarely used as reinforcing filler in tyre treads [5]. This could be the reason for the absence of carbon residue in most of the tread samples studied.

From Table 1, all the studied materials demonstrate a comparable composition of elements. It signifies that all materials contain the right proportion of organic atoms for tyre treads. However, to differentiate the elements according to the specific constituents used in tread manufacturing, i.e., natural rubber, styrene-butadiene rubber, etc., is not possible by elemental analysis. The rubber constituents are common because of their identical atoms that building up the polymer although each of them having dissimilar molecular structures.

Figure 1 displays the SEM images of the recycled materials. The morphology varies according to the physical nature of the materials. For the slab compounds, Sh-PT reveals a smoother and uniform surface when compared to Sh8(2) and Sh9(2). This could be attributed to the process (operating conditions) from which the compound is made and/or the ratio of the constituents used in the blend. It is noted that both Sh8(2) and Sh9(2) are made from the whole tyre, and it is postulated that the cracks and rough surface are due to impurities, undesired substances and/or incorrect formulation that are associated with the use of the whole segments of recycled tyre. For 40-mesh powdered samples, AP40 exhibits a smoother surface as compared to the other similar counterparts. Accordingly, it is estimated that the quality of AP40 is comparable to that of Sh-PT.



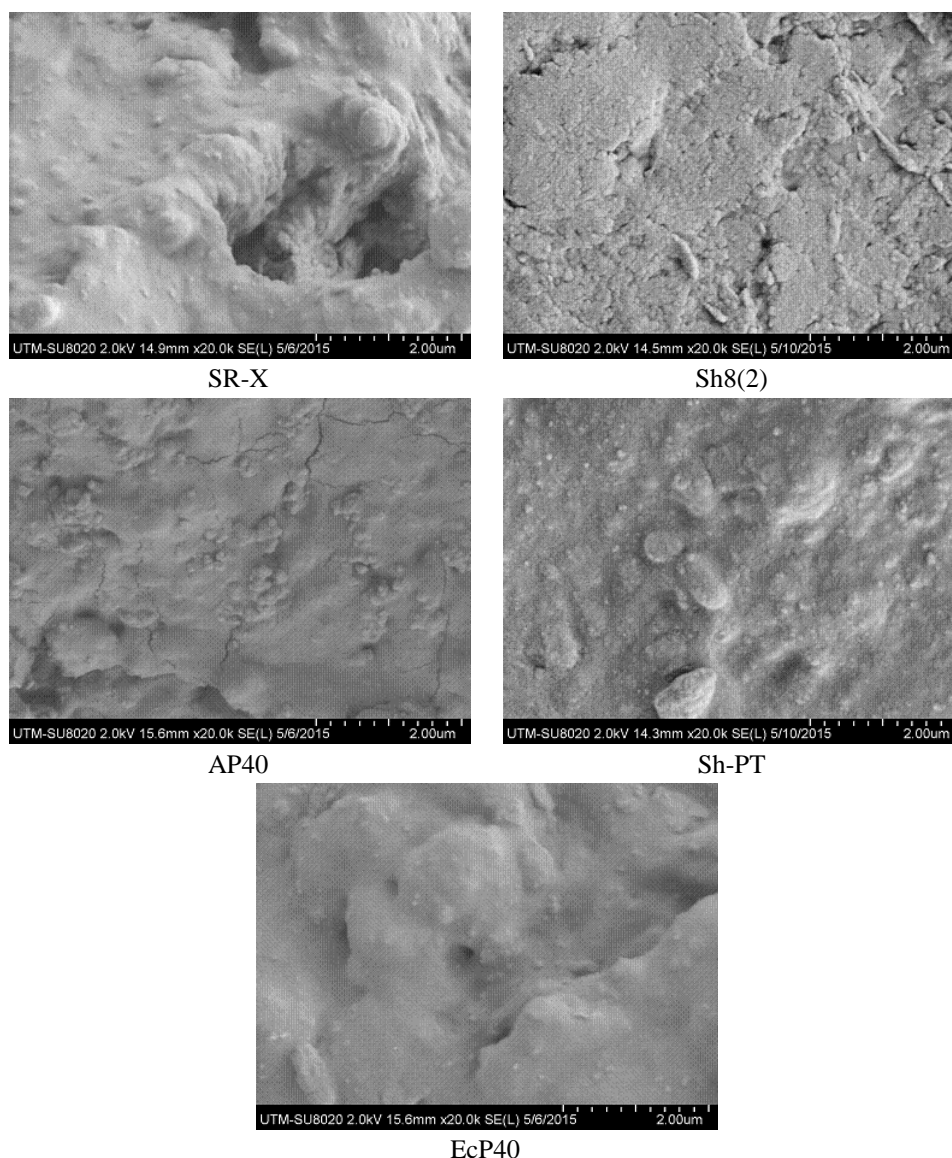


Figure 1. SEM images of tyre tread compounds

Table 2 summarizes the surface composition by EDX. In general, the data shown in Table 2 are in agreement with the elemental composition as reported in Table 1. The composition of carbon on the surface of each material varies from 75% to 100%. A 100% carbon content signifies the absence of other elements on the material surface. The EDX data also reveal that the possible constituents of ash are zinc and silica. The absence of oxygen and inorganic constituents in some of the tread compounds as detected by EDX as opposed to the data presented in Table 1 may indicate that the distribution of elements in tread compounds is not uniform throughout the material matrix.

Table 3 summarizes the oil content in the recycled materials. The values are ranging from 2% to 6%, i.e., the normal limit of oil amount used in conventional tyre to facilitate the processing of rubber compounds [6]. Oil is also used in tyre as an essential ingredient towards the technical performance, particularly for the road grip properties [2]. However, as far as the tyre tread is concern, the addition of oil should be kept minimum to meet the desirable proportion of natural rubber. In addition, the requirement to withstand overheating and wear resistance is more

important than wet grip [3]. The oil content obtained through this method was also compared with the approximate determination using a TGA at 350 °C.

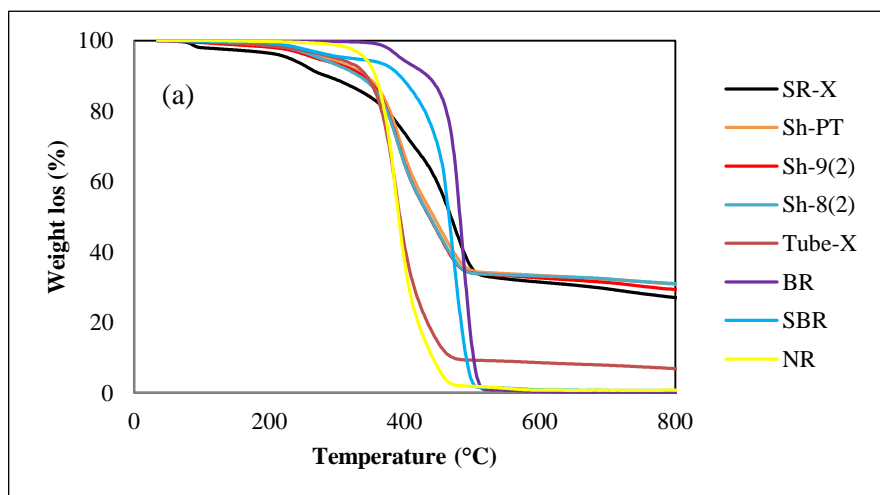
Table 2. Surface analysis by EDX

Generic ID	Carbon	Oxygen	Sulphur	Zinc	Silica
SP40-X	86.7	6.5	3.4	3.3	-
SR-X	97.1	-	2.9	-	-
AP40	100	-	-	-	-
EcP40	96.9	-	3.1	-	-
Sh9(2)	100	-	-	-	-
Sh8(2)	75.4	15.7	3.3	4.7	0.9
Sh-PT	100	-	-	-	-

Table 3. Oil content in the recycled tyre tread compounds

Generic ID	Oil Content (%)
SR-X	5.78
Sh-Pt	5.59
Sh-9(2)	3.67
Sh-8(2)	4.40
Tube-X	2.07
AP-40	2.63
ECP-40	4.30
SP40-X	2.55

Figure 2 shows the heating patterns of the recycled tyre tread compounds. The predicted breakdown of constituents is tabulated in Table 4.



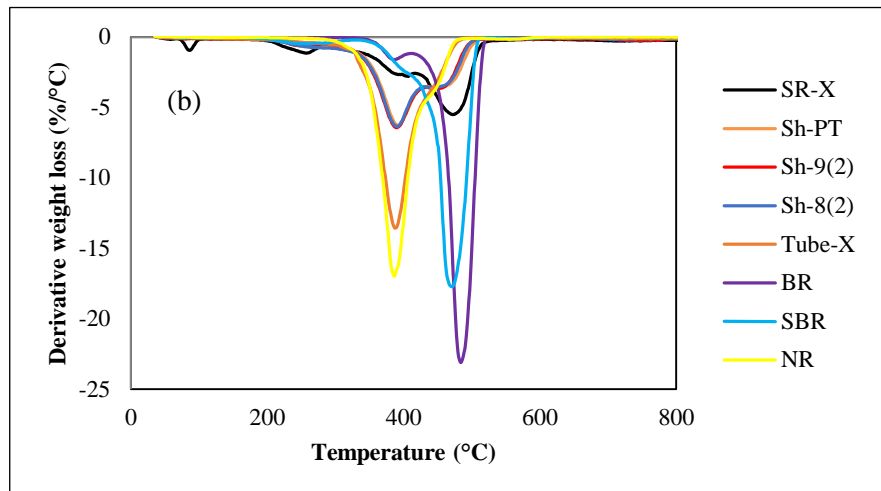


Figure 2. Thermogravimetric profiles: (a) TG and (b) DT curves

Table 4. Mass balance-thermogravimetric approach to estimate the composition of tread compounds

Generic ID	Oil wt.% at 350 °C	Carbon Black+Fillers wt.% at 515 °C	NR wt.% at 350-435 °C	NR wt.%	SBR wt.% (by diff.)	%NR Polymer	%SBR Polymer
NR	7.5	0.0	79.8	92.5	0.0	100.0	0.0
SBR	0.7	0.0	0.0	0.0	99.3	0.0	100.0
SR-X	16.2	33.3	19.5	22.6	27.9	44.7	55.3
Sh-Pt	11.2	34.2	36.1	41.8	12.8	76.6	23.4
Sh-9(2)	12.0	33.7	37.5	43.5	10.8	80.1	19.9
Sh-8(2)	12.9	33.7	36.5	42.3	11.1	79.2	20.8
Tube-X	12.0	9.2	68.6	79.5	0.0	100.0	0.0
AP40	11.2	37.3	42.8	49.6	1.9	96.3	3.7
EcP40	13.7	35.7	38.6	44.7	5.9	88.4	11.6
SP40-X	11.3	36.2	43.8	50.8	1.7	96.7	3.3

From Figure 2, it is obvious that each reference material (NR, BR and SBR) possesses distinct heat decomposition profile with sharp peak at different temperatures. Such dissimilarity can be used to predict the intrinsic composition of each rubber sample. As a matter of fact, oil is the first component that is released or decomposed upon heating at 300-350 °C [7]. Therefore, the first portion of weight loss in thermogravimetric profile at 350 °C is assumed to be that of oil. The oil content by this approximation method is nearly two to five times greater than that obtained using a conventional hexane extraction. It should be noted that oil readily exposed on the surface is most likely to be extracted, while certain amount of oil within the material matrix could be inaccessible to the solvent. Thus, the amount of oil obtained through solvent extraction is often inaccurate unless the compound has already been cut into small pieces to increase the contact area for extraction. While, the thermogravimetric relies on the boiling point of component, hence it is more reliable to represent the fraction of oil that is liberated upon heating. Nevertheless, cautions should be exercised as the given value could be misleading due to the small mass (30-100 mg) used in the TGA analysis.

SR-X exhibits some fraction of moisture, and a higher oil content that is easily vaporized at lower temperature as depicted by peaks at about 85 °C and 250 °C, respectively. The second portion of weight loss that generates sharp peak is due to the presence of natural rubber. The natural rubber (NR) displays a peak centred at 387 °C. Materials having a considerable fraction of NR (>70%) also display a similar peak but with different intensities depending on the amount of NR used in the tread compounds. It can be estimated that the weight loss from 350 °C to 435 °C directly corresponds to NR, and the value is then corrected to 100 % NR. For example, Tube-X that possesses similar intensity of peak as NR contains 79% NR, 12% oil and 9% carbon black and filler. The percentage of polymer in Tube-X is therefore 100% NR. The calculations are based on simple mass balance by integrating the peaks in the thermogravimetric profiles.

From Figure 2, there is a gradual weight loss for all recycled materials at temperature above 515 °C. The remaining weight could be assigned to the amount of carbon black and fillers (Zn and/or Si). It is evident that there is no amount of carbon black and filler in NR, BR and SBR, while Tube-X contains 9.2% carbon black and filler. On the other hand, other materials demonstrate a comparable amount of carbon black and filler, ranging between 34% and 37%. The difference between the amount of carbon black and filler can be established using BS EN 12879:2000 (heating at 850 °C for 2 h under air flow), i.e., the same method used to determine ash content. The TGA approach could also be used to determine the carbon black content through stepwise heating by switching the N<sub>2</sub> flow to air flow from 700 °C onwards [8, 9]. This is due to the fact that carbon black is somewhat resistant to heat and possesses slow degradation under N<sub>2</sub> flow as shown in Figure 2.

It is obvious from Figure 2 that most of the recycled materials display a secondary peak that is tallied with that of SBR. Hence, it is assumed that the remaining polymer in the tread compounds is SBR. The fraction of SBR in the compounds can be calculated by difference. From the mass balance calculation, SR-X demonstrates a considerable fraction of SBR of 55%. To validate the mass balance-thermogravimetric approach, some samples were analyzed using an in-house method of RRIM, and the findings are summarized in Table 5. The in-house method of RRIM yields a close agreement with the proposed mass balance-thermogravimetric approach (Table 4). It shows that the thermal degradation profiles could be sufficiently used to differentiate the types of rubber, and also to quantitatively estimate the composition of polymers used in the tyre tread compounds.

Table 5. Composition of tread compounds using an in-house method of RRIM

Composition	SP40-X	AP40	EcP40	Sh9(2)
NR (%)	90	90	70	70
BR (+SBR) (%)	10	10	30	30
Polymer (%)	57.5	57.8	54.2	60.3
Carbon black (%)	30.2	29.9	29.4	27.3
Ash (%)	5.6	5.6	5.3	5.3
Solvent extract (%)	6.7	6.7	11.1	7.1
Zinc oxide (%)	1.7	1.6	1.0	1.2
Total sulfur (%)	2.4	2.2	1.8	2.4
TMQ (%)	0.1	0.1	0.1	0.1

Figure 3 shows the FTIR spectra of the recycled tyre tread compounds, and the respective peaks assignments are summarized in Table 6. All tread compounds demonstrate a similar pattern of FTIR spectra. The peaks shown in Table 6 correspond to the common structure of rubber; long chain aliphatic (single bond) hydrocarbons, alkenes or aromatic (double bond), and sulfur groups (used in vulcanization). In addition, the presence of alkenes and aromatic could not be distinguished because both of them fall under the same wave number of 1300-1500 cm<sup>-1</sup>. Thus, it is

rather difficult to identify as whether the tyre tread compounds contain either SBR or BR. Moreover, this approach is purely qualitative, and is only sufficient to estimate the surface functional groups.

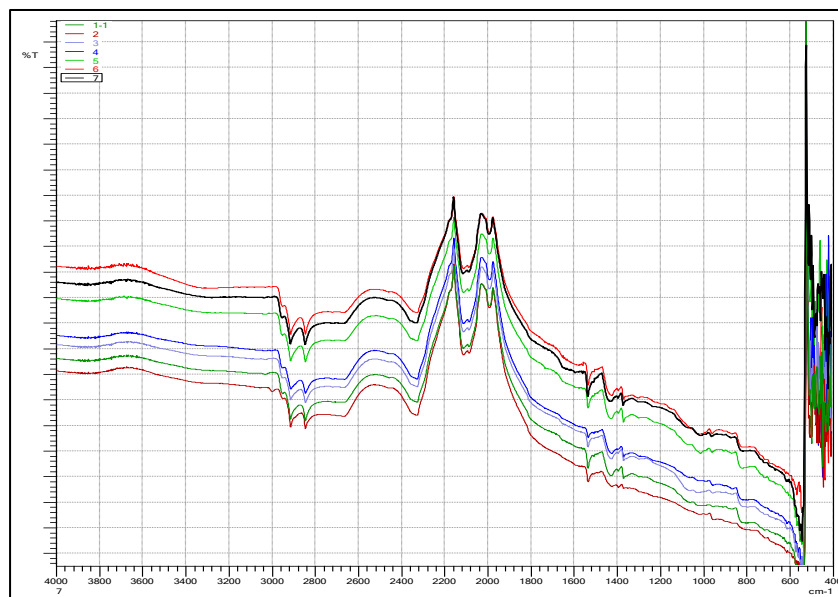


Figure 3. FTIR spectra of tread compounds

Table 6. Peaks assignments

Wavenumber (cm <sup>-1</sup> )	Assignment	1. SP40-X	2. SR-X	3. AP40	4. EcP40	5. Sh9(2)	6. Sh8(2)	7. Sh-PT
705-570	Disulfides, C—S stretch	548	556	542	548	538	542	538
1500-1300	C—H bending vibrations (alkenes)	1537, 1372, 1431	1537, 1396	1537, 1429, 1372	1535, 1427, 1371	1535, 1429, 1373	1535, 1425, 1371	1535, 1396, 1373
2150-1990	Isothiocyanate (—NCS)	2114, 1994	2116, 1991	2114, 1992	2114, 1990	2114, 1994	2116, 1990	2114, 1992
2700-2400	Thiols and sulfides (S—H)	2328	2328	2328	2328	2328	2326	2332
2865-2845	Methylene, C—H symmetric stretching vibrations	2847	2847	2847	2847	2847	2847	2847
2935-2915	Methylene, C—H asymmetric stretching vibrations	2916	2914	2914	2914	2914	2914	2914



Figure 4 shows the profiles of dielectric properties of tread compounds at varying frequencies. The values of dielectric constant,  $\epsilon'$  and loss tangent,  $\tan \delta$  at 2.45 GHz are summarized in Table 7.

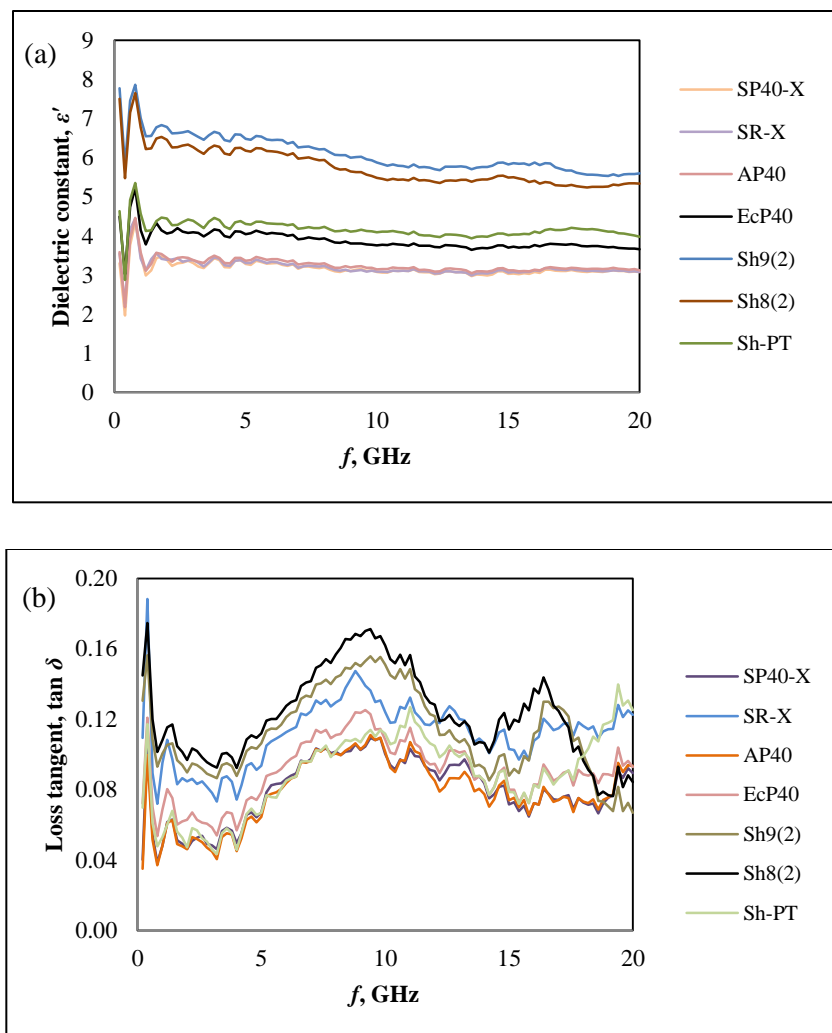


Figure 4. (a) Dielectric constant and (b) loss tangent of tread compounds at varying frequencies

Dielectric constant determines the behaviour of the material under microwave radiation. It includes how much energy is reflected from the material, as well as how efficient is the material to store the microwave energy. On the other hand, the loss tangent describes the efficiency of a material to dissipate the stored energy (microwaves) as heat [10]. In general, the compounds exhibit high dielectric constant and loss tangent compared to the pristine rubbers (Table 7). Although there are differences in the values of dielectric constant and loss tangent, all rubber samples display a comparable pattern of dielectric properties. It indicates that the materials are made from the same major constituents that are microwave-transparent [10]. Because rubber is not a dielectric material, the deviation in values could be attributed to the use of ionic salt (ZnO) in the material [11]. Nevertheless, this method seems unsuitable to distinguish the composition of polymers used in the compounds.

Table 7. Dielectric constant and loss tangent of tread compounds at 2.45 GHz

Sample	$\epsilon'$	$\tan \delta$
BR	2.65	0.02
NR	2.18	0.02
SBR	2.17	0.02
SP40-X	3.30	0.05
SR-X	3.40	0.08
AP40	3.44	0.05
EcP40	4.11	0.06
Sh9(2)	6.63	0.09
Sh8(2)	6.26	0.10
Sh-PT	4.35	0.05

### Conclusion

The recycled tyre treads were characterized to evaluate the composition, and to determine a suitable and quick approach to estimate the quality of the compounds. A simple mass balance-thermogravimetric approach was proposed to estimate the composition of oil, natural rubber and fillers, and that of SBR can be calculated by difference. The ash content can be obtained through heating at 850 °C for 2 hours, and its constituents can be predicted using EDX. The results were validated, and show a good agreement with the in-house methods of RRIM. Other characterization outcomes such as FTIR spectra and dielectric properties, however offer insufficient information towards the quality of tread compounds. The mass balance-thermogravimetric approach provides a quick and reliable assessment of the composition and quality of recycled tyre tread compounds.

### Acknowledgement

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