

Original Research Paper

Decalin Dissolving Method for Recover of Styrene –Butadiene Rubber from Scrap Tires

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Abstract: Decalin, a hydrocarbon industrial solvent was used for the recovery of Styrene- Butadiene Rubber (SBR) from grind scrap truck tires using chemical dissolving method. The applied technique is easy, simple and depends on available materials. The method depends mainly on steeping the scrap tires grind into decalin at 50°C for one month. Then the process was followed by boiling of the formed thick black solution (198°C) for two hours. The formed elastic rubber material will be reclaimed by precipitation in methanol. The recovered rubber was characterized using FTIR spectroscopy and XRD analyses. The pattern of the recovered material shows broad maxima of SBR with the absence of XRD peaks of carbon black and almost all the other tire manufacturing additives. The thermal characteristics of the reclaimed rubber have been investigated by TGA, DTG and DSC analyses and were found to be close to those of thermal properties of SBR polymer. The SEM image has shown non-crystalline morphological surface of the recovered rubber with cohesive elastomeric properties.

Keywords: SBR Reclaims, Decalin Dissolving Method, Scrap Tires, Steeping Method, Recycling

Introduction

The world consumes 4.5 million tons of tires, in addition to billions of tires of different types are to be disposed of in the USA. This huge amount of scrap tires is a big concern as ecological pollution problem (Czajczynska *et al.*, 2017). While it could be used as an alternative source of energy if this scrap is transformed into useful material. This scrap consists of about 60-65% rubber (Martinez *et al.*, 2013) and the rest are different additives and fillers. Therefore, isolation of the rubber from the other additives should be a valuable way to obtain a useful material which could be processed and reused in several industrial procedures.

Several process have been developed for tires recycling. Pyrolysis of the scrap tires under vacuum was extensively used to produce tire-derived oils that may be used as fuel or added to conventional fuels in order to reduce the dependence on the limited fossil oils (Murugan *et al.*, 2009). However, most methods of rubber recovery from the scrap were found unsatisfactory since many treatments lead to ecological problems and insufficient pure rubber recovery (Umeki *et al.*, 2016). In many countries inappropriate disposal of the scrap tires is done by incineration in the open fields, which causes dramatic pollution problem.

Vehicle tires are made of rubber after vulcanization with sulfur to render it crosslinked and after adding several additives, like fillers, steel wires, plasticizers, extenders accelerators, curing agents and others in order to improve their mechanical, thermal and physical properties. This complicated structure makes rubber recovery quite a difficult task (Mastral *et al.*, 1999; 2000).

Decalin, is an industrial hydrocarbon solvent used for dissolving resins and can be blended with other hydrocarbons solvents to be used as high density rocket ramjet and turbojet fuels (Bryant and Burdette, 1978 - US Patent 4,099,931). Decalin was used in thermal degradation of HDPE polymer (Aguado *et al.*, 2006) where it could facilitate the degradation process and had a significant effect on the product distribution. Decalin participates in the degradation mechanism and effects the degradation time and temperature significantly (Aguado *et al.*, 2007). Decalin has hydrogen donating ability as solvent has been investigated as a method for the feedstock recycling of plastic wastes.

Decalin a bicyclic saturated hydrocarbon was used in the present work as solvent for reclaiming the rubber from scrap tires. Decalin has the ability to penetrate into the tire materials, swell them and finally extract the rubber out. The work includes treatment of the scrap

tires with decalin and the extracted rubber was studied carefully using spectral, XRD, thermal analysis. SEM images were used to see any differences between pristine tire and its recovered rubber.

Experimental

Materials

Truck scrap tires were supplied from the local market. The tire samples were prepared by cutting into pieces, cleaned and grinded. Decalin from BDH Chemical Company, UK was used without further purification. Methanol from Fluka, Switzerland was used as received.

Decalin Steep of Scrap Tire for a Long Time

10 g of grinded scrap tire were steeped in 100 mL of decalin in a conical flask and the flask was heated on water bath at 50°C for 30 days.

Rubber Recovery Procedure

After 30 days steeping the solution turned into black color with a thick texture. This black thick solution was then transferred into 250 mL round bottom flask connected to condenser and was refluxed for about 3h at the boiling point of decalin (198°C) using mantel and in presence of boiling chips. The solution, was left to cool. The separation of undissolved suspended materials, which are mainly carbon black, was carried out using ultra centrifuge at 13000 rps. Methanol (43% v/v) was added for precipitation separation of rubber however, since methanol is not miscible with decalin because of their polarities, the mixture was spread in Petri dish inside an oven at 30°C until dried. A thick white layer with rubbery texture was collected. The separated carbon black could be used after washing with methanol.

Characterization of Recovered Rubber and Pristine Tire Samples

FTIR Spectrophotometry

FTIR spectra were recorded on a Fourier-Transform Infrared spectrophotometer model S8400 from Shimadzu Company, Japan. The spectra were measured in the spectral range 400-4000 cm^{-1} .

X-Ray Diffraction (XRD) Analysis

X-ray diffraction measurements of the recovered rubber and a pristine sample were recorded at a scan of 1 min^{-1} using XRD -600/Shimadzu/Japan) using copper Indium (0.9/0.1) 100% radiation target and nickel filter at a current 20 μA under a voltage of 35 kv.

Thermal Measurements

Thermogravimetric (TG), Differential Thermogravimetric (DTG) analyses and Differential

Scanning Calorimetry (DSC) of only the recovered rubber sample was measured using TG instrumental type METTLER TOLEDO (Switzerland) micro and ultra – micro balances, under nitrogen atmosphere at a heating rate of 10°C/min in the temperature range of 25-600°C.

Scanning Electron Microscopy

SEM images of the recovered rubber and the untreated scrap tire samples were mounted on aluminum studs using double adhesive taps and coated under vacuum by exposing to a gold ion beam sputter. The type of SEM instrument used was TESCAN-VEG/USA.

Proton Nuclear Magnetic Resonance (^1H NMR) Measurement

^1H NMR of rubber sample of the recycled material of scrap tire extracted by decalin has been investigated and its structure was analyzed by ^1H NMR using the instrument Bruker Biospin GmbH of 400 MHz spectrometer frequency. Where the samples dissolved in CDCl_3 solvent and measured at room temperature.

Results and Discussion

Most recycling processes of the scrap tires depends on either incineration for energy reclaims; pyrolysis to oil for an alternative fuel for diesel engines; crumbed the tires for flooring indoor arena, or the tires were recycled by shredding and filled cement composition for certain infrastructural applications. In general, most treatments are not directed for reclaiming rubber from the scrap tires. The present work concentrates on recovery of rubber from scrap tires in a form that can be reused again.

Characterization of the Recovered Rubber

The pristine scrap tire sample before treatments has been characterized and compared with the recovered rubber.

FTIR Study

The absorption frequencies of scrap and recovered rubber samples are including in Table 1 and Fig.1.

In general, the spectra show that the sample mainly consists of hydrocarbon groups, The band at 3080 cm^{-1} represents $\gamma(\text{C-H})_{\text{str}}$ of aromatic ring and $\gamma(\text{CH}_2)_{\text{str}}$ aliphatic. The absorption frequency at 1452 cm^{-1} represents $\gamma(\text{C-H})_{\text{def}}$ and $\gamma(\text{C}=\text{C})_{\text{str}}$ of aromatic ring, beside the peak at 1069 cm^{-1} of $\gamma(\text{C-H})$ in the plane, representing those for the spectrum of polystyrene (Leon-Bermudez and Salazar, 2008). In addition, the absorption frequencies at 1630 cm^{-1} and 1660 cm^{-1} belong to $\gamma(\text{C}=\text{C})$ of the aliphatic chain of butadiene (Munteanu and Vasile, 2005).

Table 1: FTIR wave numbers of the characteristic bands of pristine scrap tire and recovered rubber samples

Examined sample	Wave number characteristic bands (cm ⁻¹)								
	γ (C-H) _{str} aromatic ring	γ (C-H) _{str} aliphatic	γ (C=C) _{str} aromatic ring	γ (C=C) _{str} aliphatic	γ (C-H) _{def} (C=C) _{aromatic}	γ (C-H) in the plane	γ (C-H) _{st} aliphatic	γ (C-H) wag	γ (C-H) twist
Pristine scrap tire	3080	2843 2920	1731	1630 1660	1452	1069	1196	910	520
Recovered rubber	γ (C-H) _{str} alkenyl	γ (C-H) _{str} alkyl	γ (C=C) alkene	γ (CH ₂) _{def}	γ (C=C) aromatic ring	γ (CH=CH) _{str}	γ (C-H) in the plane	γ (C-H) alkenyl	
	3024 3059	2849 2924	1601 1678	1493	1448	1373	1070	758 903 960	

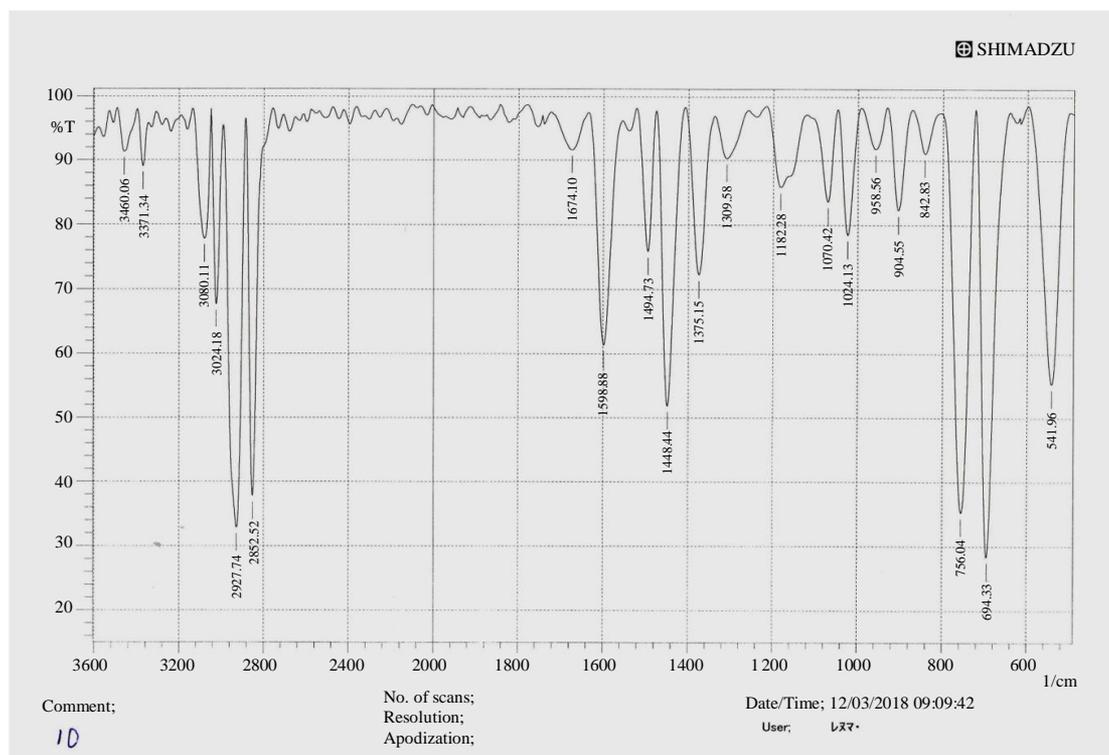


Fig. 1: FTIR spectra of pristine scrap tire sample

Table 1 and Fig. 2 of the decalin recovered rubber sample have shown almost the same Previous mentioned bands. Where the absorption frequencies at 1448 cm⁻¹ and 1070 cm⁻¹ represent γ (C=C) aromatic ring and γ (C-H) in the plane, respectively, which are the main functional groups of the polystyrene present in the recovered rubber. The characteristic bands γ (C=C) of alkene and γ (C-H)_{str} of alkyl and alkenyl all belong to the butadiene moiety in the recovered rubber.

X-Ray Diffraction Analysis

The XRD pattern of pristine scrap tire Fig. 3 has shown that the examined material is non-crystalline with a very broad maxima 10° to 20° along 2θ axis, including some intense peaks. Those peaks belong to reinforcing

filling inorganic materials and quantities of other additives (Chatterjee and Khobragade, 2017).

In general, the XRD pattern of the pristine scrap tire gives valuable information about the homogeneity of the sample which consist of different organic and inorganic materials mixed with rubber.

The X-ray diffraction of the recovered rubber shown in Fig. 4 has a broad maxima starts from 8° to 24° along 2θ axis which represents the SBR. The small maxima between 8° to 12° represents the polystyrene and that from 15° to 24° along the 2θ axis represents the polybutadiene in SBR (Essawy *et al.*, 2012). While the sharp maxima peaks at 42°, 44.8° and 49° represent the few organic additives present in the sample.

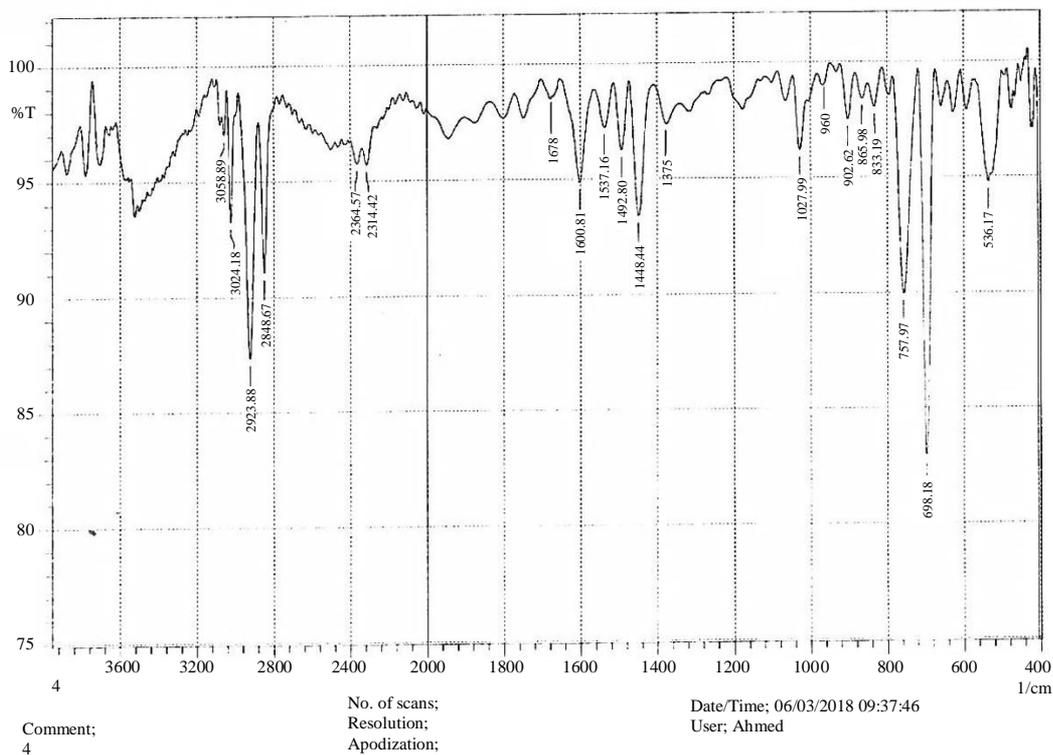


Fig. 2: FTIR spectra of recovered rubber from scrap tire sample treated with decalin

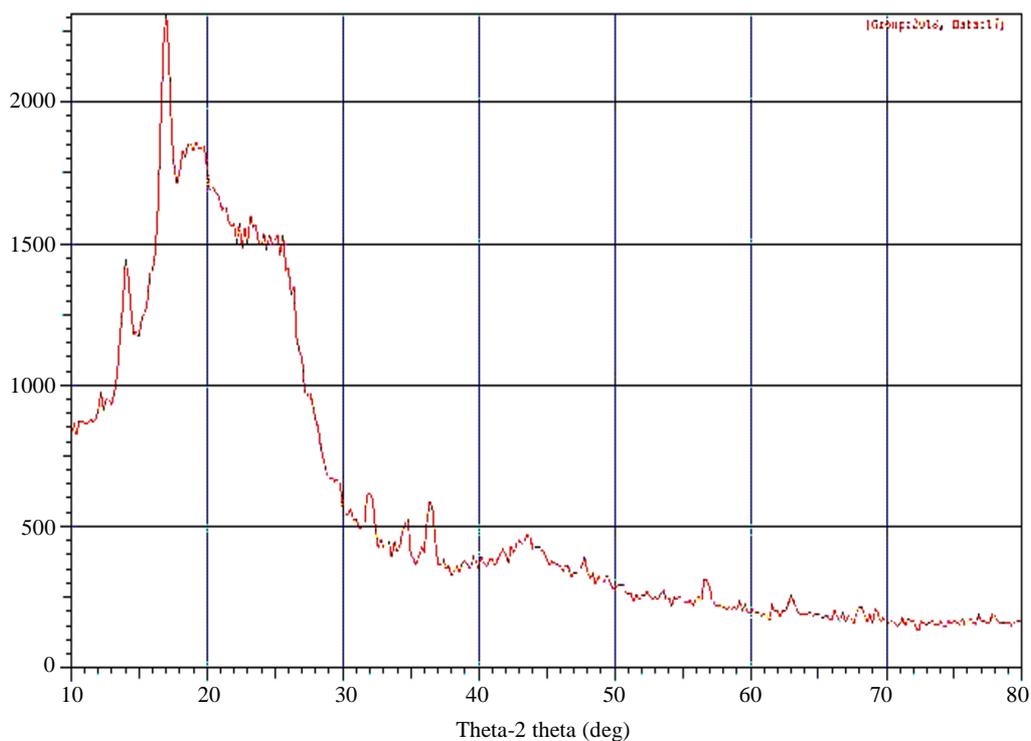


Fig. 3: XRD pattern of the scrap tire sample

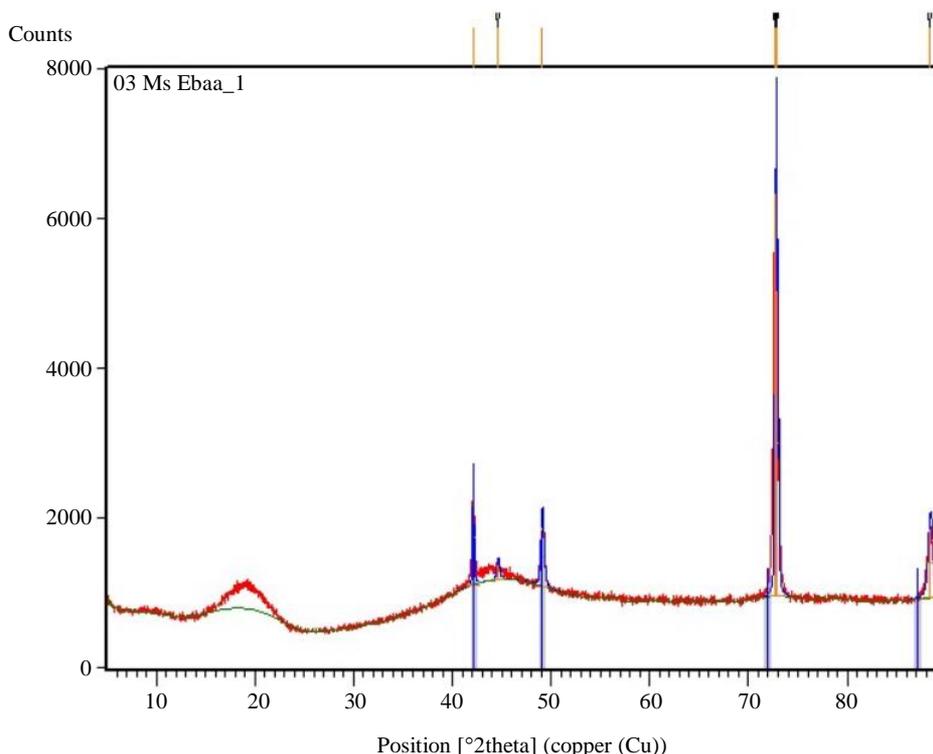


Fig. 4: XRD pattern of recovered rubber from scrap tire sample treated with decalin

Table 2: TG, DTG, DSC thermal parameters of decalin recovered rubber

TG thermogram			DTG thermogram		DSC thermogram	
Thermal parameter	Weight loss%	Temp. °C	Rate of decomp. (mg min ⁻¹)	Temp. °C	T _g °C	ΔH _f J.mg ⁻¹
IDT	6.0	290	0.17	418	>0	+47.2
FDT	100.0	450				
T _{max}	47.0	405				-2.34
T _{cr}	98.5	435				

Thermal Analysis

TGA, DTG and DSC thermal analysis of the decalin recovered rubber were studied and their thermal parameters are displayed in Table 2. The TGA-thermogram in Fig. 5a shows the Initial Decomposition Temperature (IDT) of 6.0% weight loss at 290°C and 100% weight loss at the Final Decomposition Temperature (FDT) at 450°C. The thermal parameters in Table 2 have shown that the decalin recovered material is thermally stable and its parameters are close to the parameters of styrene-butadiene rubber (Rybinski *et al.*, 2013). The DTG-thermogram Fig. 5b, Table 2 display the maximum rate of decomposition of decalin recovered rubber of 0.17 mg min⁻¹ at 418°C.

In general the rate of decomposition per minute is very low which means that the recovered rubber is thermally very stable (zhang *et al.*, 2014).

The DSC-curve of the recovered rubber in Fig. 5(c) records the heat of fusion ΔH_f of +47.2 J.mg⁻¹ with the appearance of a little magnitude of exothermic heat fusion of -2.34J.mg⁻¹ which may belong to the double bond decomposition of polybutadiene. Accordingly, the DSC- thermogram parameters give indications that the decalin recovered rubber is certainly styrene-butadiene rubber (Anyszka *et al.*, 2016).

SEM Analysis

The SEM images of the pristine scrap tire sample in Fig. 6 show homogeneity of the tire components

with some distributed cavities which look as black regions in the SEM image. The whitening spots distributed uniformly along the sample representing the carbon black filler. Moreover, the pristine scrap tire shows homogeneous sample present in elastic form and has molar cohesion which comes from the vulcanization process that gives the sample the

visible folds, cavities and holes (Munteanu and Vasile, 2005).

The SEM image of decalin recovered rubber in Fig. 7 has shown a cohesive elastic surface containing folds and has large holes. The absence of whitening regions means the sample has no crystalline morphology and has rubbery texture.

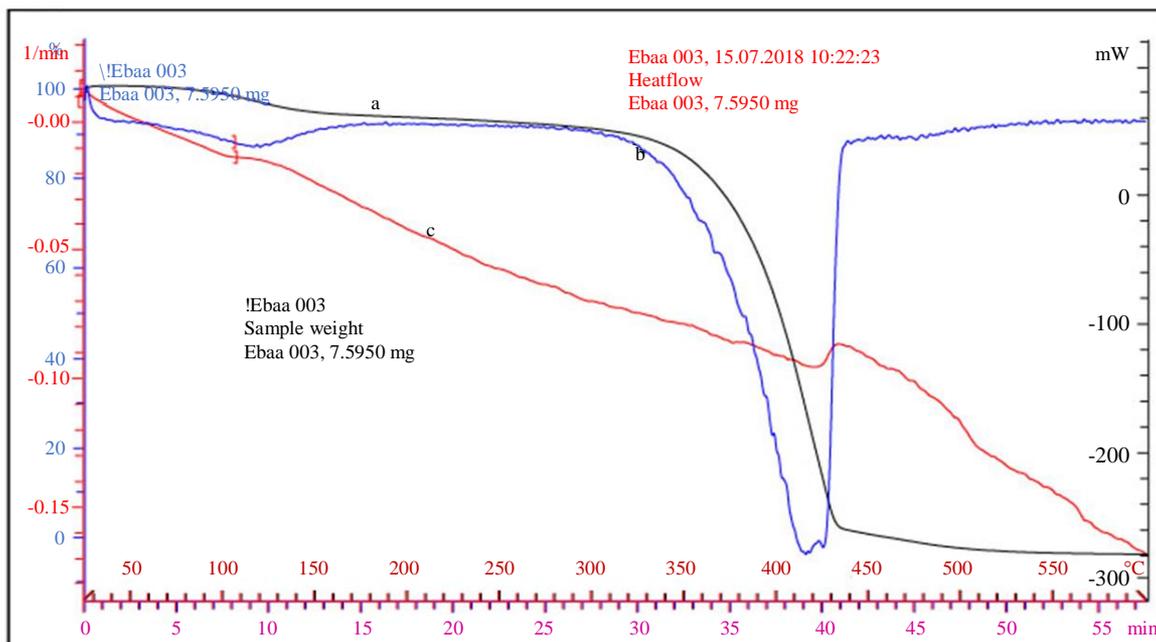


Fig. 5: (a) TGA (b) DTG (c) DSC thermogram of recovered rubber from the scrap tire sample extracted by decalin

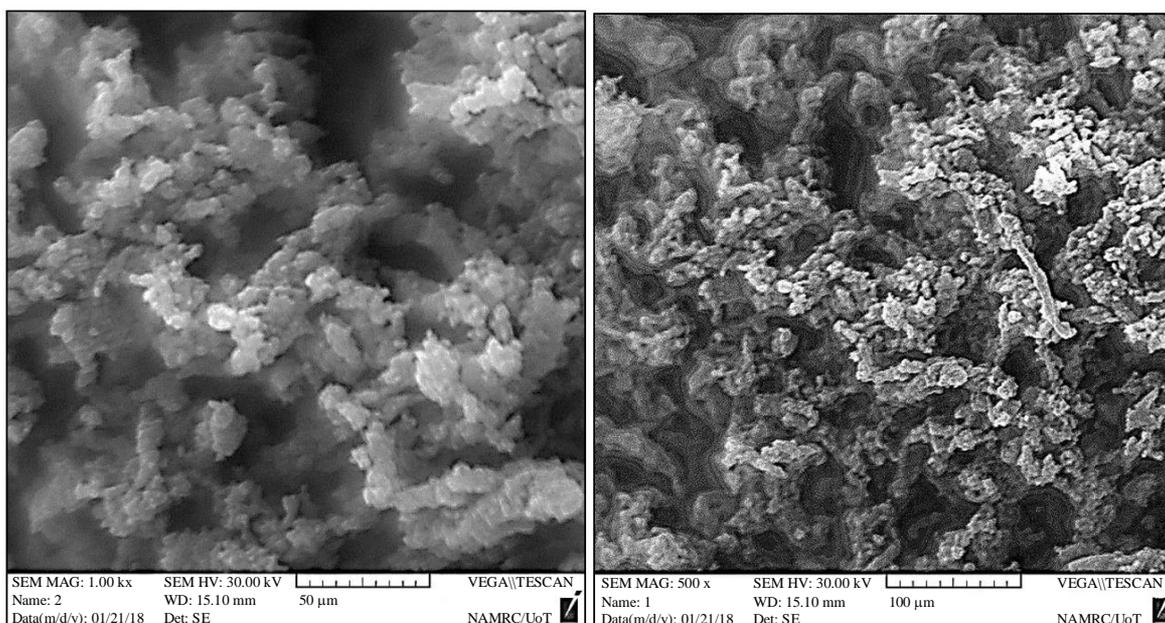


Fig. 6: SEM image of pristine scrap tire

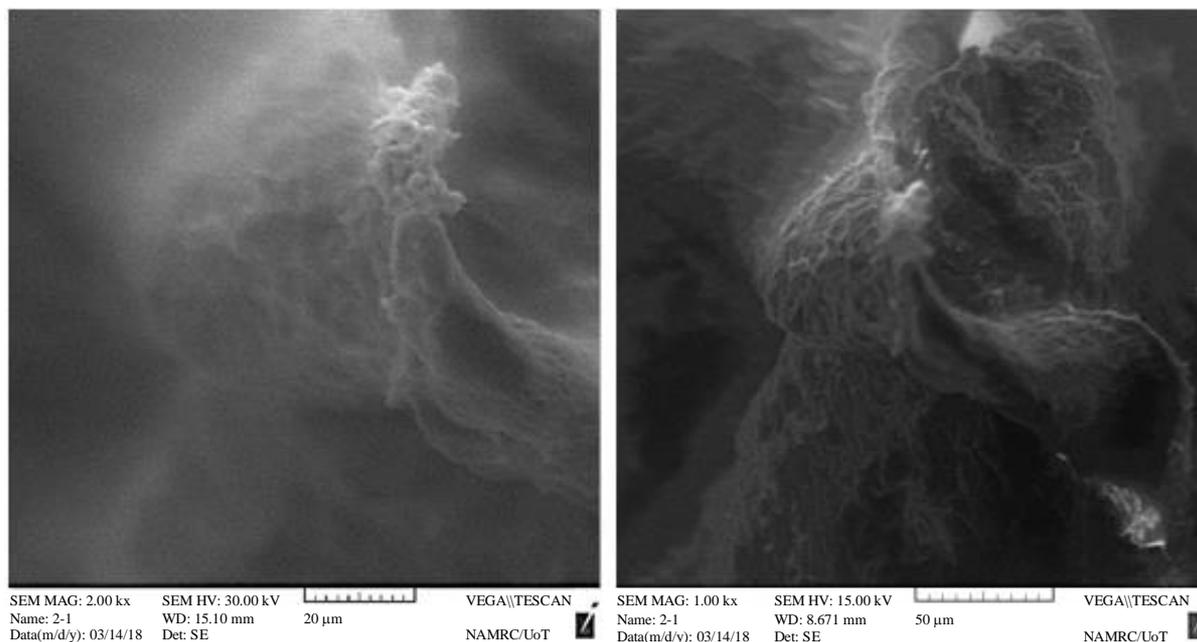


Fig. 7: SEM micrograph of the recovered rubber

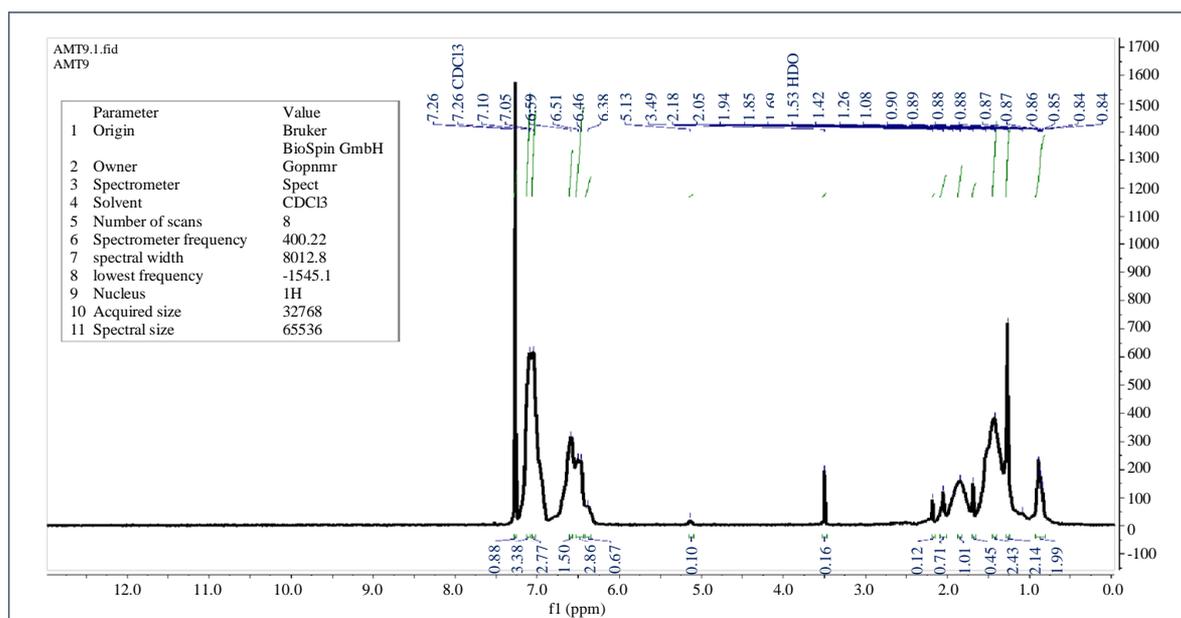


Fig. 8: ¹H NMR spectrum of recovered rubber from scrap tire extracted by decalin

¹H NMR Analysis

The recovered rubber from grind scrap tire using decalin was examined by ¹H NMR analysis using 400MHz, Bruker spectrometer and CDCl₃ as deuterated solvent. The Fig. 8 has shown resonance of (2H, m) at (3.49 and 5.13) ppm represent unsaturated ethylene group of the natural rubber.

Beside the resonance of (2H, m) of methylene protons which belong to natural rubber. Styrene has shown resonance of (5H, m) at (7.05-7.26) ppm represents aromatic protons of styrene ring. Finally, the compound have a resonance of (5H, m) appeared at (6.38-6.59) ppm which represent aliphatic protons of styrene-butadiene main chain of the rubber.

Conclusion

The final white recovered rubber which was extracted from scrap tires using decalin solvent was characterized with different sophisticated analysis in order to ascertain its composition.

The FTIR spectroscopy analysis show the main functional groups of the polystyrene γ (C=C) aromatic ring and γ (C-H) in the plane, beside γ (C=C)_{str} of the alkene belonging to polybutadiene rubber, thus indicating that the recovered rubber has styrene-butadiene rubber structure.

The XRD pattern of the recovered rubber show broad maxima which start from 8° to 24° on the 2 θ axis is too much closer to the broad maxima of the non-crystalline styrene butadiene rubber. Moreover, the disappearance of peaks after 24° means that decalin had extracted only rubber from the grind scrap tire and leaving the other additives. The thermal parameters of decalin recovered rubber give indication that the extracted material is thermally stable and its rate of decomposition is low and that its thermal parameters indicate that the material is styrene-butadiene rubber. The SEM image of the recovered material has shown morphological surface of rubber texture with cohesive elastic surface. The ¹HNMR has shown the final recovered rubber was SBR.

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Author's Contributions

Aeppa Mohammed Taher Sultan: Contributed in collection of literature and for carrying out experimental work.

Fawzi Habeeb Jabrail: Contributed in analysis, discussing and interpreting of the data. He also participated in writing and checking of final review of the draft.

Ethics

Both authors have read and approved the manuscript and there are no ethical issues associated with this research. This article is original and contains unpublished materials.

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