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Spectroscopic, thermal, impedance and hardness studies on uncured and cured Silicon rubber

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Abstract: The present work is entirely devoted to the characterization of uncured and cured Silicon rubber. The effect of sulphur and carbon black on the property of rubber material was studied using important experimental techniques. The complete vibrational band assignment made for the rubber material confirms its chemical structure. Further, thermal behavior of the rubber material essential for proper processing and fabrication was studied from Thermogravimetric Analysis (TGA). Activation energy for the degradation of rubber materials was calculated using Murray-White and Coats-Redfern plot. Also, the hardness of Silicon rubber in the raw and cured state was determined using Shore A durometer.

Keywords: cured Silicon; FTIR; thermal behavior; Activation energy; hardness

I. INTRODUCTION

The chemical analysis of rubber is an important guide to its value. The tests of the physical properties of rubber usually applied to determine its value in the market has become very important. The development of the rubber industry has now reached a stage at which more exact methods of determining the chemical composition and physical properties of rubber are required. Silicon rubber was investigated in its uncured and cured state for systematic characterization by employing important experimental techniques. Vulcanization is the treatment of rubber to give it certain qualities, e.g., strength, elasticity and resistance to solvents and to render it impervious to moderate heat and cold. For many uses, even vulcanized rubbers do not exhibit satisfactory tensile strength, stiffness, abrasion resistance and tear resistance. Therefore, the rubber has to be compounded with reinforcing fillers before vulcanization in order to obtain vulcanizates with adequate mechanical properties known as reinforcement. The thermal behavior of chlorinated natural rubber, masticated natural rubber and a blend of these two polymers have been studied by J.W. Cook et al [1]. Jean Le Bras et al reported the significance of the chemical interaction between carbon black and elastomer interface [2]. According to P. Thavamani et al, the thermal stability of EVA was improved on blending it with HNBR [3]. N. Rattanasom et al have studied reinforcement of NR with silica/carbon black hybrid filler at various ratios in order to determine the optimum silica/carbon black ratio [4]. Liliane Bokobza et al have reported recent investigations on filled natural rubber [5]. Naba K. Dutta et al have investigated the dynamic mechanical and physical properties of BIIR to determine the effect of particle size and structure of carbon black and silica [6]. According to Daniel P. Kowalik et al., carbon black filled silicon can be used as a compliant thermoelectric material as it was found to exhibit absolute thermoelectric power of $+2 \mu\text{V}/^\circ\text{C}$ [7]. The present research work deals with the characterization of Silicon rubber by employing FTIR, TGA, and hardness studies. Thus a sincere attempt has been made to study the structure-property relationship of the rubber material.

II. EXPERIMENTAL METHODS

Silicon rubber was procured from Industrial Rubber Products (IRP), Chennai, India for systematic characterization. Carbon black was used as the reinforcing filler and sulphur was used as the principle-vulcanizing agent in the industrial lab. After proper mastication, the rubber material was passed through the rolls of the roll mill equipment. The combined cure package comprises the cure agent sulphur together with accelerators like Dibenzothiazyl disulfide (MBTS) and Tetra Methylthiuram Disulfide (TMTD), activators like zinc oxide and stearic acid and antidegradants according to the desired formulations. Antidegradants were used

to prevent degradation by heat, oxygen and ozone. The composites were vulcanized at 160°C under a pressure of about 45 kg/cm². The time of vulcanization was 30 minutes. The reinforced rubber materials were obtained by mixing carbon black filler to the vulcanizates in the roll mill equipment [8]. The carbon black filler content was 50 Phr (Phr-parts hundred in rubber). After the rubber, filler, sulphur and organic accelerator were mixed; the compound was placed in molds and subjected to heat and pressure. The heat was applied directly by steam. The rubber article was intended to adopt the shape of the mold. The samples were obtained in the form of slabs with thickness about 8 ± 0.5 mm. Infrared spectroscopic analysis of Silicon rubber was carried out with Bruker IFS 66V spectrophotometer at Indian Institute of Technology (IIT), SAIF, Chennai, India. The FTIR spectra have been recorded in the range 4000 - 400 cm⁻¹ and the frequencies of all the sharp bands are accurate to ± 1 cm⁻¹ [9]. For recording IR spectra, the rubber sample was cut into small pieces and taken in a boiling tube. The contents were subjected to conditions of high temperature and pressure so as to bring them to semi liquid state. A drop of this liquid was smeared to form a transparent film between two circular NaCl disks. The NaCl disks with the sample film were placed in the IR cell and the spectra was recorded.

Thermogravimetric Analysis was carried out in a high-resolution thermobalance (NETZSCH STA 409C/CD instrument) at Indian Institute of Technology (I.I.T), Chennai, India. Approximately 5mg - 6mg of rubber sample was heated from room temperature to 1400°C with a continuous circulation of nitrogen gas inside the sample and reference chamber. The heating rate is 20°C/min but when a loss of weight is detected for the sample in the high-resolution TGA technique, the heating rate slows in response to mass and the system tries to keep it at the lowest value (0.01°C/min) until the end of weight loss. The sample weight and its rate of weight loss continuously measured as a function of temperature was used to calculate activation energy for the degradation of rubber samples.

The hardness of raw and vulcanized Silicon rubber was measured using a Shore A Durometer. The Durometer is an International Standard instrument used to measure the hardness of rubber materials. The greater the hardness of the material, the greater resistance it has to deformation. Durometers measure hardness by the penetration of an indenter into the rubber sample. The instrument is a spring loaded indentation device, in which values are obtained as a function of the viscoelastic property of the material. The calibrated reading is expressed in a number value. The truncated cone indenter extends to 0.098 inch (2.5 mm) and is pressed on to the sample against an 822g spring. Each 0.001 inch of deflection of the indenter is shown as 1 degree shore (A). Samples used were 8mm thick with a surface area sufficient to permit at least 3 test points 5mm apart, 13mm from any edge. The standard method for determining the hardness of rubbers is given in ASTM 1415-88, BS 903-A57 and DIN 53505 [10].

III. RESULTS AND DISCUSSION

A. FTIR Spectroscopy

The vibrational spectrum of a molecule is considered to be a unique physical property and is characteristic of a molecule. The FTIR spectra of Silicon rubber in the raw and cured state is given in Fig. 1. The spectra are nearly identical and confirm that the polymeric units are the same for the elastomers in the raw and cured state except for minor differences. A quantitative analysis of structure and confirmation of polymer chains requires the assignment of absorption bands and qualitative measurement of their intensities. The assignments of the fundamental frequencies have been made on the basis of magnitude and relative intensities of the observed bands. The vibrational band assignments of the rubber materials have been made in correlation with molecular composition and with their indices of stereo regularity [11]-[12].

The frequencies of the elastomers with their relative intensities and probable assignments are summarized in Tables 1 and 2. On comparison of raw and cured states of the rubber material, it can be stated that the difference is in their rate of absorption only. The process of vulcanization is considered to introduce cross-links between the polymer molecules due to addition of sulphur. Since the infrared spectrum of an elastomer is determined almost entirely by the small recurring structural units and not by the gross size or configuration, the net result of vulcanization, consisting mainly of changes which involve relatively few of the recurring polymer units, does not alter the rubber spectrum to any appreciable extent [13]. As the spectrum of each elastomer is unique and experimentally reproducible; this serves as a basis for characterization of the elastomer content of commercial rubber products.

Figure 1 FTIR spectra of (a) Silicon rubber (b) cured Silicon rubber

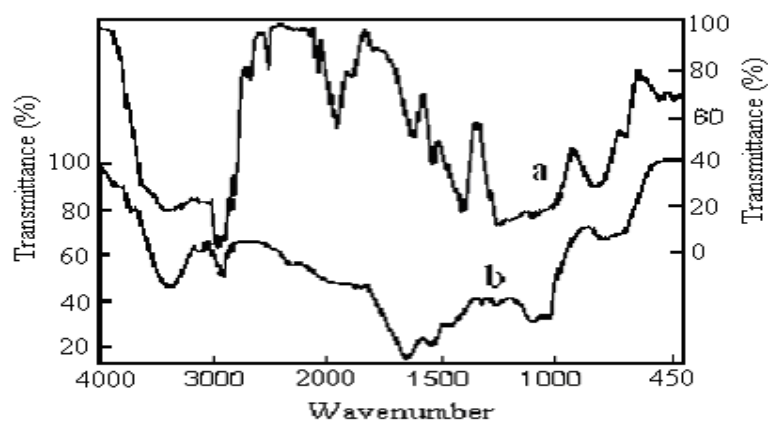


Table 1 SPECTRAL ASSIGNMENT OF RAW SILICON RUBBER

Frequency (cm^{-1})		Assignment
FTIR	Intensity	
3060	s	C-H asymmetric stretching
2964	vs	C-H symmetric stretching
2914	vs	CH ₃ asymmetric stretching
2842	s	CH ₃ symmetric stretching
1413	s	CH ₃ asymmetric bending / Si-CH ₃ asymmetric
1342	mw	CH ₃ symmetric bending
1254	vs	Si-CH ₃ symmetric bending
1107	s	Si-O-Si symmetric stretching
821	s	CH ₃ rocking / Si-C stretching

vs-very strong s-strong mw-medium weak

Table 2 SPECTRAL ASSIGNMENT OF CURED SILICON RUBBER

Frequency (cm^{-1})		Assignment
FTIR	Intensity	
3020	m	C-H asymmetric stretching
2950	m	C-H symmetric stretching
2917	ms	CH ₃ asymmetric stretching
2855	m	CH ₃ symmetric stretching
1468	s	CH ₃ asymmetric bending / Si-CH ₃ asymmetric
1360	ms	CH ₃ symmetric deformation
1259	s	Si-CH ₃ symmetric deformation
1097	s	Si-O-Si asymmetric stretching
1019	s	Si-O-Si symmetric stretching
797	mw	CH ₃ rocking/Si-C stretching

s-strong ms-medium strong mw-medium weak m-medium

B. Thermogravimetric Analysis (TGA)

Knowledge of thermal behavior is not only essential for proper processing and fabrication, but also for complete characterization of materials especially thermal stability and for selection of appropriate end users. The sample weight and its rate of weight loss were continuously measured as a function of temperature. The thermal stability was determined from TGA curves as given in Table 3. The thermal behavior of Silicon rubber is an unique one [14]-[15]. The thermal degradation is multistage showing weight losses of 32%, 20%, 2.1% and 1.5% in the first, second, third and fourth stages respectively. The TGA thermogram shows a weight loss of 10% at 468°C and 50% at 570°C. Only 57% of silicon rubber was degraded at 1400°C. The TGA curve of silicon (v) shows that the degradation process is single stage. About 56% of the rubber material was degraded in this stage between 380°C to 610°C. The sample has undergone 30% degradation at 532°C and 60% degradation at 723°C. It is evident from the TGA thermogram that 41% of the rubber sample remains undegraded. Hence both raw and cured silicon are found to be thermally stable materials. [15] Reported that the conductive silicon rubber filled with conductive carbon black has better thermal stability than that of silicon rubber without any fillers. Activation energy is the minimum amount of energy that is required to activate atoms or molecules to a condition in which they can undergo chemical transformation or physical transport. Activation energy calculations for the degradation of rubber materials were made from TGA curves using Murray-White method and Coats-Redfern method [16]-[17]. The calculation of activation energy for the degradation of cured Silicon rubber is given in Table 4. A linear correlation was obtained by plotting the logarithm of heating rate against the reciprocal of the absolute temperature [18]. In Murray and White plot, a linear correlation was obtained by plotting $T^{-1} \times 10^{-3} (K^{-1})$ against $[\ln(\ln(1-C)-2\ln T)]$. In Coats and Redfern plot, a linear correlation was obtained by plotting $T^{-1} \times 10^{-3} (K^{-1})$ against $\log [\ln(1-C)]/T^2$. The calculated activation energy values are given in Table 5. Cured silicon has high activation energy and is more thermally stable [19]. The extent of polymerization, chain length and hence the molecular weight will be more for the elastomers that are less stable. It can be concluded that thermal stability i.e., the ability to maintain required mechanical properties such as strength, toughness and elasticity at a high temperature is more for cured silicon than raw silicon rubber.

Table 3 THERMAL STABILITY OF RUBBER MATERIALS

Sample	Temperature (°C) corresponding to weight loss								
	10%	20%	30%	40%	50%	60%	70%	80%	90%
Silicon	468	506	529	548	570	-	-	-	-
Cured Silicon	472	512	532	549	568	723	-	-	-

Table 4 CALCULATION OF ACTIVATION ENERGY FOR CURED SILICON

% Degradation	$T^{-1} \times 10^{-3} (K^{-1})$	1-C	2lnT	ln(1-C)	log[ln(1-C)]	$\frac{\ln[\ln(1-C)]}{2\ln T}$	$\frac{\log[\ln(1-C)]}{T^2} \times 10^{-6}$
10	1.3422	90	13.226	4.4998	0.6531	-11.7227	1.176
20	1.2738	80	13.331	4.3820	0.6416	-11.8538	1.041
30	1.2422	70	13.381	4.2484	0.6282	-11.9351	0.969
40	1.2165	60	13.423	4.0943	0.6121	-12.0139	0.905
50	1.1890	50	13.469	3.9120	0.5923	-12.1051	0.837
60	1.0040	40	13.807	3.6888	0.5668	-12.5021	0.571

Table 5 ACTIVATION ENERGY FOR DEGRADATION OF RUBBER MATERIALS

Sample	Activation energy E_a in KJ/mol	
	Murray-White Method	Coats-Redfern Method
Silicon	0.4846	0.5522
Cured Silicon	0.546	0.653

C. Hardness of Rubber Materials

The usual method to achieve a hardness value is to measure the depth or area of an indentation left by an indenter of a specific shape, with a specific force applied for a specific time. The greater the hardness of the material, the greater resistance it has to deformation. The rubber materials used for the hardness study were rectangular in dimension with 8mm thickness. The hardness of the rubber material is obtained by forcing the standard indenter of the Shore A durometer onto a flat surface of rubber material and measuring the degree of penetration. The deflection of the pointer in the durometer scale directly gives the hardness of rubber materials. It is observed that cured Silicon has a hardness value of 62 than compared to 28 for uncured one. This shows the intense effect of sulphur and carbon black on the rubber material [20]-[21]. The hardness of the rubber material is enhanced after being vulcanized with sulphur and reinforced with carbon black.

IV. CONCLUSION

The cured and uncured Silicon rubbers were successfully characterized by utilizing important experimental techniques. Spectroscopic investigation on the rubber material has been made through infrared studies and the results have been briefly discussed. A complete vibrational band assignment has been made available for raw and cured silicon rubber. From TGA thermograms, activation energy was calculated for the degradation of rubber material using Murray-White method and Coats-Redfern method. Cured Silicon rubber exhibits better thermal stability than the unvulcanized raw silicon rubber. Hardness measurements reveal that cured Silicon rubber exhibits greater hardness than the uncured one.

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