J. Rubb. Res., **16(2)**, 75-90

Effect of the Blooming of Chemical Curatives on the Dynamic Behaviour of Silanised Silica Filled Natural Rubber-to-metal Bonded Bobbins

F. SAEED[*#], A. ANSARIFAR[**], R. J. ELLIS[***] AND Y. HAILE-MESKEL[***]

Rubber is viscoelastic in nature and used in a variety of industrial applications. Rubber mounts are used to dampen vibration and shock. Damping, fatigue and dynamic properties of rubber mounts depend to a large extent on chemical ingredients mixed with the rubber. Natural rubber is the most widely used polymer for conventional mounts. Apart from natural rubber, different fillers and rubber chemicals are also present in conventional formulation of rubber mounts. Conventionally, five different classes of chemical curatives are used in rubber industries, which include curing agents, primary and secondary accelerators as well as primary and secondary activators. When chemical curatives are present in excessive amounts in rubber, they migrate to the rubber surface and form a bloomed layer.

In this work, two rubber formulations were used for preparing rubber-to-metal bonded bobbin mounts. The formulations were primarily based on natural rubber with 60 parts per hundred rubber by weight (p.h.r.) precipitated amorphous white silica nanofiller. The surface of silica was pre-treated with bis(3-triethoxysilylpropyl)-tetrasulphane (TESPT) coupling agent to chemically bond silica to the rubber. The rubber was cured primarily by reacting the tetrasulphane groups of TESPT with the rubber chains using a sulphenamide accelerator and the cure was then optimised by adding zinc oxide as an activator. The ratio of the accelerator to activator in one compound was 6 p.h.r./0.3. p.h.r. and the compound showed extensive blooming of the accelerator on the rubber surface when stored at ambient temperature for up to 60 days. However, the blooming was reduced significantly by changing the ratio of the accelerator to activator to 3 p.h.r./2.5. p.h.r., which was subsequently used to prepare a second compound.

Dynamic and static properties of the bobbins were subsequently measured. Both compounds showed very low phase angle (δ) and spring rate ratio K_d/K_s (K_d: dynamic spring rate; K_s: static spring rate). Notably, the compound with the high accelerator to activator ratio had superior aforementioned properties, but the dynamic fatigue life of the bobbin reduced noticeably due to a gradual deterioration of the bond caused by the migration of the accelerator to the bonded interface.

Keywords: rubber; silica; fatigue life; spring rate ratio; phase angle; bobbins

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[*] Department of Polymer and Process Engineering, University of Engineering and Technology, Lahore, 54890, Pakistan.
[**] Department of Materials, Loughborough University, Leicestershire, LE11 3TU, UK.
[***] DTR VMS Ltd, Bumpers Way, Chippenham, Wiltshire SN14 6NF, United Kingdom.
[#] Corresponding author (e-mail: F.Saeed@uet.edu.pk)

Rubbers are used to manufacture a range of industrial articles such as tyres, conveyor belts, engine mounts, bridge bearings, and suspension bushes. In service, most rubber articles undergo dynamic loading. For example in cars, engine mounts damp the vibration produced by the engine and shocks made by uneven roads while acting as an isolator between the engine and car body. As rubbers are viscoelastic in nature, deformation in rubber materials can be divided into two components, elastic and viscous. The elastic component represents the spring, which obeys Hook's law where stress and strain are in phase. When rubber is deformed under stress, energy is stored which can be recovered when stress is removed, whereas, the viscous component of the rubber represents the dashpot and stress and strain are out of phase by 90°. The energy used in a dashpot to move the force against the viscous drag cannot be stored or recovered and is lost as heat. Rubber compounds act in between the spring and dashpots[1]. For most applications, dynamic properties such as phase angle (δ), spring rate ratio (K_d/K_s), and fatigue life are crucial. Bobbins are used as vibration isolators and should have low phase angle values because a low phase angle imparts better spring like properties and low heat build-up[1,2]. The values of δ and K_d/K_s depend on the type of rubber, fillers and cure systems used. Both δ and K_d/K_s values increase when filler loading in the rubber compound is increased[3].

Fatigue life represents the durability, reliability, and safety of the manufactured rubber components[4,5]. Fatigue life of rubber components depends on mechanical loading, rubber formulation, and environmental conditions that include temperature, oxygen level, ozone level and electrostatic charges[6]. Apart from the above mentioned conditions, blooming of the chemical curatives can also have a detrimental effect on the fatigue life of rubber components. Some studies have shown that migration of chemical curatives through natural rubber to the surface, damaged the internal structure of the rubber by creating flaws which then reduced the cyclic fatigue life of the rubber vulcanisate[7]. Excessive use of the chemical curatives produced solid agglomerates and weakened resistance to crack growth in natural rubber under dynamic loading. This in turn increased the rate of crack growth at a constant level of tear energy and caused a faster failure of the rubber vulcanisate under repeated stressing[8]. Blooming of the chemical curatives also had a detrimental effect on the surface adhesion properties of natural rubber[9,10].

The aim of this study was to investigate effect of the blooming of a sulphenamide accelerator on the dynamic behaviour of some rubber-to-metal bonded bobbins. The bobbins were made from natural rubber filled with 60 parts per hundred rubber by weight (p.h.r.) of a silanised silica nanofiller. The hardness, tensile strength, modulus (M100), specific gravity and elongation at break of the cured rubbers were measured. The phase angle, spring rate ratio and fatigue life of the bobbins were also measured soon after the bobbins were stored at room temperature (~ 21°C) for up to 60 days to allow full blooming of the accelerator on the surface of the bobbins to occur.

EXPERIMENTAL

Materials

The raw rubber used was Standard Malaysian Rubber grade L (SMR L) containing 98 wt % 1-4 *cis* content. The reinforcing filler was Coupsil 8113, which was supplied by Evonik Industries AG (Essen, Germany). Coupsil 8113 is a precipitated amorphous white silica type Ultrasil VN3 surface of which had been pretreated with *bis*(3-triethoxysilylpropyl-)-tetrasulphane (TESPT), also known as Si69 coupling agent, to chemically bond silica to

rubber. It has 11.3% by weight silane, 2.5% by weight sulphur (included in TESPT), a 175 m^2/g surface area (measured by N_2 adsorption), and a 20 – 54 nm particle size.

In addition to raw rubber and filler, other ingredients were N-tert-butyl-2-benzothiazole sulphenamide (TBBS; a safe processing delayed action accelerator with a melting point of 109°C) (Santocure TBBS, Flexsys, Dallas, TX), zinc oxide (ZnO; an activator, Harcros Durham Chemicals, Durham, UK) and N-(1,3-dimethylbutyl)-N′-phenyl-p-phenylenediamine (6PPD, an antidegradant with a melting point of 45°C, Santoflex 13, Brussels, Belgium). The melting temperatures of ZnO and silanised silica are above 1000°C. The cure system consisted of TBBS and ZnO, which were added to fully crosslink the rubber.

TBBS was added to react the rubber reactive tetrasulphane groups of TESPT with the rubber chains to produce crosslinks and zinc oxide (activator) to enhance the efficiency of TBBS and optimise the cure in the rubber. In addition, the antidegradant was added to protect the rubber against environmental ageing by ozone and oxygen.

The adhesive systems used for bonding the rubber to metal were Chemosil 211 and Chemosil 225. Chemosil 211(grey colour) is a primer to protect the metal surface against corrosion and Chemosil 225 (black colour) is an adhesive that is applied on top of the primer layer to bond rubber to metal. Chemosils 211 and 225 contain adhesive promoting agents and rubbery phases. During the vulcanisation process, the rubbery phases and adhesive promoting agents diffuse through the interfaces between primer, adhesive and rubber layers to produce strong bonding and at the same time, the primer forms good bonding with the metal surface.

Preparation of the Rubber Compounds

The two natural rubber compounds (*Table 1*) were made in an industrial internal mixer at Eastland Compounding, UK. For preparation of the rubber compounds, a total mixing time of 16 min was used[11]. The rubber and filler were placed in the mixing chamber and mixed for 13 min, fully dispersing the silica particles in the rubber[12]. After 13 min of mixing, TBBS, ZnO and antidegradant were added and mixed for another three minutes. The rubber compounds were removed from the internal mixer and milled to a thickness of about 10 mm and wrapped up in clean plastic sheeting. The compounds were passed through the gap between the rolls of a two-roll machine once to produce the thin sheets. The compounds were then stored at ambient temperature (21 ± 2°C) for at least 24 h before their cure properties were measured.

Cure Properties of the Rubber Compounds

The scorch time, t_{s_2}, which is the time for the onset of cure and the optimum cure time, t_{95}, which is the time for the completion of cure, were determined from cure traces generated at 140 ± 2°C and 165 ± 2°C by a moving die rheometer (MDR, Prescott Instrument Ltd, Gloucestershire). The data was stored using Prescott Labline software version 2001. Tests were performed at an angular displacement of ± 3° and a test frequency of 1.7 Hz.

The cure rate index, which is a measure of the rate of cure in the rubber, was calculated using the method described previously[13]. Δtorque, the difference between maximum and minimum torque values on the cure trace of the rubber which indicates crosslink density changes[14], was calculated from the cure traces. The rheometer tests ran for up to 1.5 hours. These measurements were carried out at the DTR VMS Ltd. testing laboratories in the UK.

Preparation of Rubber Test Pieces and Bobbins

After the rubber compounds were stored at ambient temperature for at least 24 h, they

TABLE 1. FORMULATIONS AND MDR TEST RESULTS OF THE NATURAL RUBBER COMPOUNDS USED TO MAKE THE BOBBINS

	Compounds	
	1	2
Formulation (p.h.r.)		
NR (SMR L)	100	100
Silanised silica	60	60
TBBS	6	3
ZnO	0.3	2.5
Santoflex 13	1	1
ODR results at 140 °C		
Δtorque (dN m)	80	68
Scorch time (min)	9	10
Optimum cure time (min)	27	53
Cure rate index (min^{-1})	5.6	2.3
ODR results at 165 °C		
Δtorque (dN m)	27.8	15.8
Scorch time (min)	2	1.5
Optimum cure time (min)	8.86	9.12
Cure rate index (min^{-1})	14.58	13.14

were then cured in an electrically heated hydraulic press at 165°C to produce thin sheets ~ 2.8 mm thick. The sheets were then used to cut suitable samples to measure tensile strength, elongation at break, modulus (M100) and specific gravity of the rubber vulcanisate. To make the bobbins, the metal inserts were first degreased by an organic solvent and then coated with the primer (Chemosil 211). After the primer fully dried off, a top coat (Chemosil 225) was applied on top of the primer. When the top coat dried off, metal inserts were placed in the cavity of a transfer mould which was heated to 140°C. The rubber compound was placed in the transfer pot and a plunger was placed on top of the rubber. The whole assembly was then placed under pressure in a hydraulic press which was heated to 140°C. Whilst under pressure, the rubber was transferred from the transfer pot into the mould cavity through the sprues and left to cure fully. After curing, the bobbins were recovered from the moulds and kept at ambient temperature for up to 60 days before durability tests were performed. Dimensions of the bobbin are given in *Figure 1*.

Note that the bobbins were cured at a lower temperature of 140°C because the rubber was thick. Therefore, a lower temperature and a longer cure time were required to ensure that heat transferred efficiently and fully into the centre of the rubber to avoid under cure.

Tensile Properties, Specific Gravity and Hardness of the Rubber Vulcanisates

The tensile strength, modulus at 100% strain amplitude (M100), elongation at break and specific gravity were measured according to the following *BS 903 - A2:1995.*

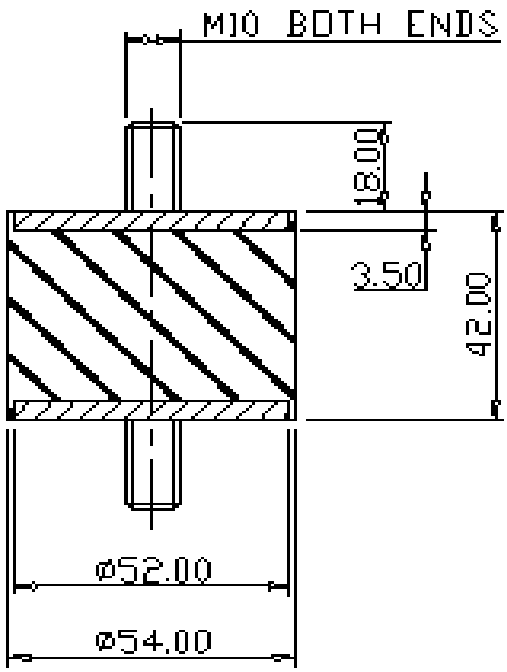

Figure 1. Dimensions of the bobbins. All the measurements are in mm.

Hardness. The Cogenix, IRHD, Dead Load Hardness tester, Model H14 with 2.5 mm indenter (The Wallace Instruments, UK) was used for measuring the hardness of the rubber vulcanisates. Cylindrical samples 12 mm thick and 28 mm in diameter were cured at 165°C and used for this test at ambient temperature (20 ± 2°C). Samples were then placed in the durometer for a 15 s time interval and a final reading was taken and expressed as international rubber hardness degrees (IRHD) value. The test was repeated at three different positions on each sample and median of the three readings was subsequently indicated[15].

Durability Tests of the Bobbins

The Deltalab-Nene's servo-hydraulic testing machine (Deltalab-Nene Ltd, Northants, UK) was used for measuring the durability of the bobbins made from compounds 1 and 2. The tests were carried out at room temperature (21 ± 2°C). The bobbins were mounted on the testing machine at zero pre-load. The experiments were performed at a test frequency of 5 Hz with a maximum applied strain amplitude of ±7 mm (20% compression and 20% extension). The standard configuration of the Deltalab-Nene testing system allows simultaneous reading and storage of two main input channels that is two signals that are read to determine the dynamic properties of the components being tested. These channels are normally "load" and "displacement", where "displacement" refers to the movement of the test machine and "load" to the reaction of the sample to the movement.

The Deltalab-Nene software (Deltalab-Nene Ltd, Northants, UK) was used for storing and processing the data. On the basis of the

load and displacement data, the software worked out the secant modulus, dynamic stiffness, phase angle and spring rate ratio K_d / K_s (K_d: dynamic spring rate; K_s: static spring rate). The test sweep ranges used for these tests were 12 – 17 Hz at 1 Hz frequency step and strain amplitude of 0.5 mm, and 70 – 150 Hz at 3 Hz frequency step and strain amplitude of 0.05 mm.

For measuring the durability or fatigue life of the bobbins, the machine ran continuously until the bobbins failed. As mentioned earlier, the tests were performed after the bobbins were stored for up to 60 days at ambient temperature.

Analysis of the Rubber Chemicals and Rubber Surfaces after Bond Failure of the Bobbins by Fourier Transform Infrared Spectrometer

A Fourier Transform Infrared Spectrometer (FT-IR-8400S) (Shimadzu Scientific Instruments, USA) (FT-IR) was used to provide molecular fingerprint information in order to positively identify compounding chemical components which underwent surface migration. TBBS, ZnO, antidegradant and silanised silica nanofiller, which were the compounding ingredients, were mixed and ground with KBr powder. The mixture was poured into a chamber and pressed manually to form a semi-transparent pellet, 1 mm thick and 10 mm in diameter. The pellet was then placed in a sample holder and tested. The test produced spectra which were examined to determine the chemical components which underwent surface migration. Attenuated total reflectance (ATR) was also used to chemically analyse and identify the bloomed layer that was present on the rubber surface recovered from the bond failure of the bobbins after the dynamic testing was ended.

RESULTS AND DISCUSSION

The cure properties of rubber compounds 1 and 2 at 140°C and 165°C are reported in *Table 1*. The TBBS/ZnO ratio of compound 1

Figure 2. Difference between the surfaces of the bobbins after 60 days in storage at ambient temperature. (A) Compound 1 shows white bloom and (B) Compound 2 shows a clean surface.

was 6 p.h.r./0.3 p.h.r. and that of compound 2, 3 p.h.r./2.5 p.h.r. Compound 1 had a shorter optimum cure time because it had a higher loading of TBBS. Compound 1 also had a higher Δtorque value, which indicated a higher crosslink density than compound 2.

As stated earlier, after the cure properties were measured, both compounds were cured at 165°C in the form of thin sheets and tested within 24 hours. The bobbins were cured at 140°C and stored for up to 60 days before further tests were carried out. The bobbins were inspected regularly in storage to observe the rubber surface. After a few days, the bobbins made from compound 1 showed a white bloom layer on the surface (*Figure 2A*), whereas, the bobbins made from compound 2 remained clean and shiny and there was no evidence of the bloom when they were examined visually (*Figure 2B*). Compounds 1 and 2 were used in a separate study by the same authors, when thin rubber samples up to 2.8 mm thick were cured from these compounds and stored at ambient temperature for up to 60 days. Compound 1 showed extensive surface bloom whereas compound 2 did not. The bloom appearing on the surface of the bobbins was similar to that seen on the thin rubber sheets kept in storage for the same length of time[7,8].

Hardness and Tensile Properties of the Rubber Vulcanisates

The hardness of compound 1 was 7% higher than that of compound 2 (*Table 2*). This was due to the fact that compound 1 had a higher crosslink density as indicated by a higher Δtorque value. Also, the presence of the bloom layer on the rubber surface resulted in the increased hardness of compound 1[7]. The increased values of hardness and crosslink density resulted in a noticeably higher modulus (M 100) for compound 1 (*Table 2*). The bloom had no adverse effect on the specific gravity and tensile strength of the rubber but elongation at break was 16% lower (*Table 2*). Previous studies showed that crosslink density changes affected rubber properties. For example, hardness and modulus increased whereas elongation at break decreased when crosslink density was increased[16-18]. Our results are in line with the previous findings.

TABLE 2. HARDNESS AND MECHANICAL PROPERTIES OF THE CURED COMPOUNDS

	Compounds	
	1	2
Specific gravity	1.154	1.152
Hardness (IRHD)	84	78
M 100 (MPa)	4.85	2.93
Tensile strength (MPa)	28.62	26.6
Elongation at break (%)	458	543

Static and Dynamic Properties of the Bobbins

The secant modulus of compound 1 was 37.2 % higher than that of compound 2 (*Table 3*). Stiffness, δ and K_d/K_s are very important for the dynamic performance of rubber mounts. Apart from the filler type and cure system which affect the rubber properties, the aforementioned properties also showed strong dependency on frequency and strain amplitude[3].The dynamic stiffness, phase angle and K_d/K_s measured during the durability test of the bobbins made from compounds 1 and 2 are reported in *Table 3*. Compound 1 had a higher dynamic stiffness but a lower K_d/K_s , which made it more suitable for damping applications. The K_d/K_s of compound 2 was higher than that of compound 1 but the ratio was still towards the lower end which made compound 2 also suitable for damping applications. Dynamic stiffness and K_d/K_s had higher values at 100 Hz frequency as compared to the values recorded at 15 Hz frequency. Normally, dynamic stiffness and K_d/K_s of rubber mounts increase with frequency[19] and our results showed a similar trend. Compounds 1 and 2 both had low phase angles, *i.e.* 1.48 – 1.8° at 15 Hz frequency and 0.5 mm strain amplitude, and 9–10° at 100 Hz frequency and 0.05 mm strain amplitude, which made them suitable for the heat build-up applications. Compound 1, due to its low K_d/K_s and phase angle values would be a better choice than compound 2 for potential use in dynamic applications.

Durability Test of the Bobbins

In a previous study, compounds 1 and 2 were cured in the form of thin sheets and standard dumbbell test pieces and long rectangular rubber strips were die stamped from the sheets and tested. The cyclic fatigue life using the dumbbell test pieces and crack growth rate as a function of the tear energy using the long strip of rubber containing an edge crack were measured. The cyclic fatigue tests were performed at 100% strain amplitude and 1.4 Hz frequency in tensile tension. The results showed that compound 1 had a shorter cyclic fatigue life than that of

TABLE 3. STATIC AND DYNAMIC PROPERTIES OF THE BOBBINS MADE FROM COMPOUNDS 1 AND 2

	Compounds	
	1	2
Secant modulus (N/mm)	912	572
15 Hz frequency and 0.5 mm amplitude		
Dynamic stiffness (N/mm)	1352	1027
Phase angle (°)	1.48	1.79
K_d/K_s	1.48	1.80
100 Hz frequency and 0.05 mm amplitude		
Dynamic stiffness (N/mm)	2191	1616
Phase angle (°)	9.26	10.03
K_d/K_s	2.40	2.83

compound 2. This was due to the migration of rubber chemicals to the rubber surface, which also produced small flaws in the rubber samples, weakening the internal structure of the rubber and reducing its cyclic fatigue life[7]. It was TBBS that had migrated to the rubber surface and produced a bloomed layer. Moreover, the blooming of TBBS resulted in an increase in the rate of crack growth at a constant level of tear energy in the rubber[8]. It was concluded that the blooming of TBBS was detrimental to the cyclic fatigue life of the rubber and reduced the resistance of the rubber to crack growth under repeated stressing. Note that these compounds were used in this study to make the bobbins. The bobbins were tested under tension and compression to measure their durability (fatigue life). In total, three bobbins were tested for each compound after they were stored at ambient temperature for 1, 30 and 60 days. Eventually, all the bobbins failed at the bond during the durability tests. The durability of the bobbins, *i.e.* number of cycles to failure, was reported for both compounds 1 and 2 in *Table 4*.

There was an increase in the durability of the bobbins after the first 30 days in storage for both compounds but when the bobbins were stored for another 30 days, the durability dropped (*Table 4*). The reason for the drop might have been that the bond deteriorated with time due to damage accumulation at the bonded interface during the dynamic testing. In the case of compound 1, this was further exasperated by the possible migration of the rubber chemicals to the rubber/top-coat interface. It could also have been that the crosslink density increased in the first 30 days of storage when further bridges or links formed between the top coat and the rubber which strengthened the bond over time. It was clear from the results (*Figure 3*) that the bobbins made from compound 2 were more durable than those made from compound 1. The results showed that compound 1 had a shorter dynamic fatigue life than compound 2 (*Table 4*).

It was noted that the bobbins failed prematurely at the rubber-to-metal bonded region and there was a white bloom layer appearing on the rubber side of the bond failure (*Figure 4*). For the bobbins made from compound 1, the bond failure occurred sooner during testing. It was likely that the gradual migration of the rubber chemicals to the bonded interface could have caused poor adhesion between the rubber/top-coat and this in turn adversely affected the quality of the bond, causing it to fail. Normally, cohesive failure in the rubber is favoured rather than failure at the bonded interfaces.

TABLE 4. DURABILITY OF THE BOBBINS MADE FROM COMPOUNDS 1 AND 2 BEFORE THE FAILURE OF INTERFACE

	Compounds	
	1	2
Durability after 1 day storage time (kc)	45	112
Durability after 30 days storage time (kc)	87	117
Durability after 60 days storage time (kc)	69	75

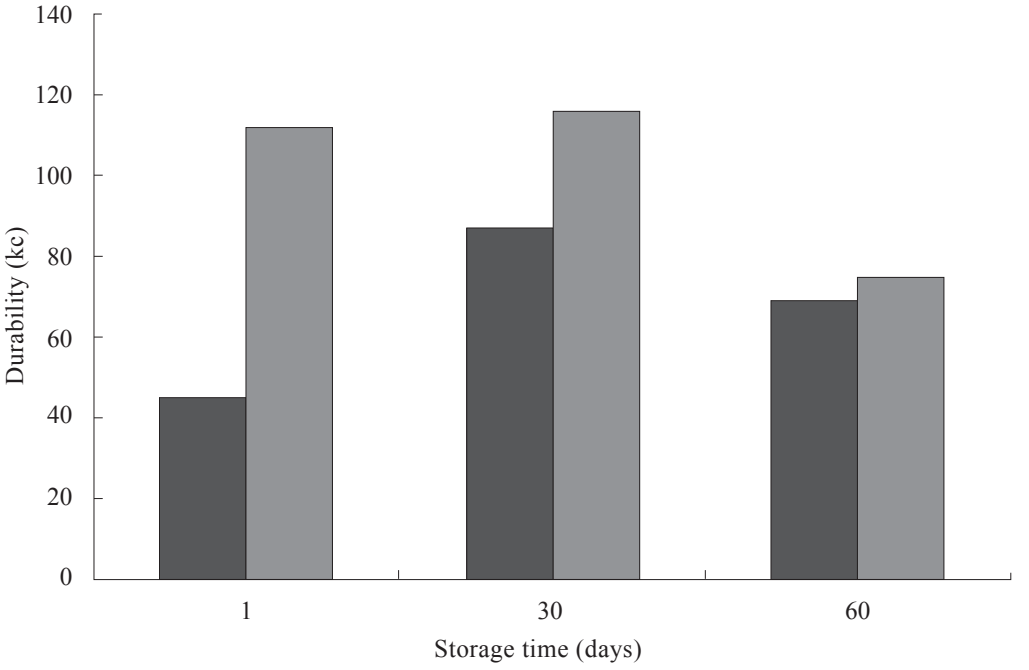

Figure 3. Comparison of the durability of the bobbins made from compound 1(■) and compound 2 (■).

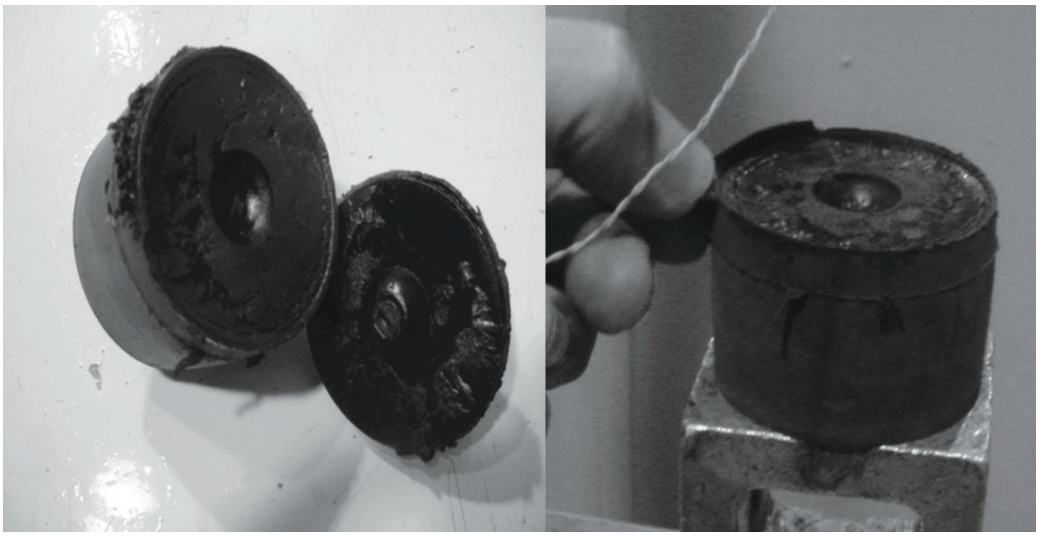

Figure 4. A typical rubber-to-metal bond failure after dynamic testing on a bobbin made from compound 1 showing extensive failure at the rubber/metal surfaces.

To investigate this further, FT-IR analysis was carried out on the rubber chemicals and ATR on the rubber surfaces after the bobbins failed.

ATR analysis of the rubber surface showed characteristic bands for TBBS at 1641.48 cm^{-1} (cf. *Figures 5* and *6*), and antidegradant at 611.45 cm^{-1}, 1028.09 cm^{-1} and 1313.57 cm^{-1} (cf. *Figures 5* and *7*) in the spectrum to indicate their presence in the bloom on the rubber surface. Notably, there were no bands for ZnO and silanised silica filler in the spectrum of the bloom (cf. *Figures 5, 8* and *9*). For ZnO, a major band at 441 cm^{-1} using FT-Raman spectroscopy has been reported[20] but FT-IR could not detect this band. The presence of antidegradant in the bloom on the rubber surface was expected since it migrated to the surface to protect the rubber against environmental ageing[21]. TBBS and antidegradant were identified to be the main compounding ingredients that had undergone surface migration.

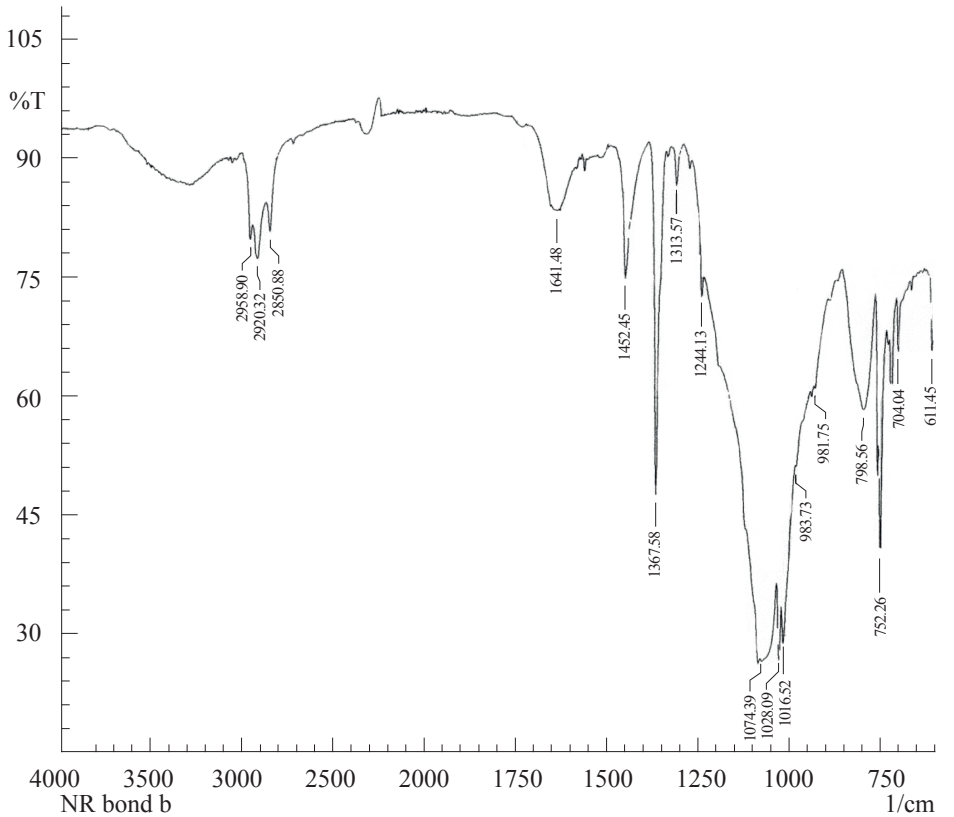

Figure 5. A typical ATR spectrum of the white bloom on the surface of rubber after bond failure.

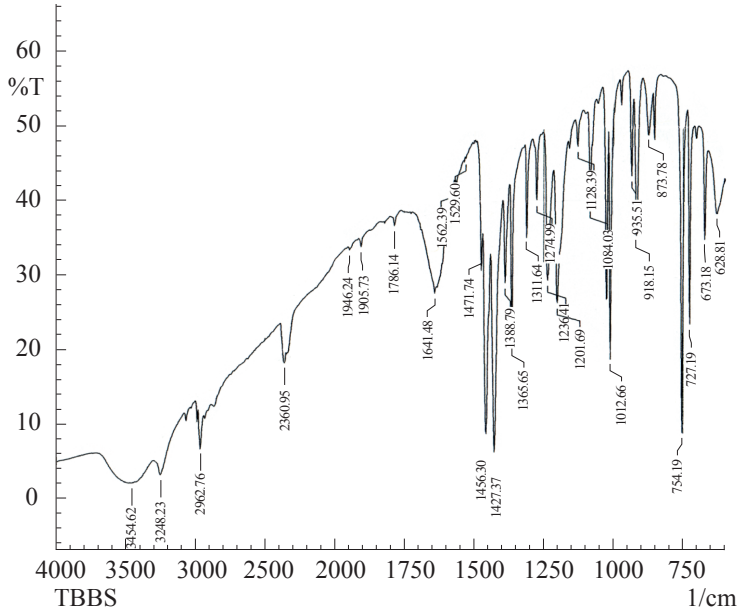

Figure 6. FT-IR spectrum of the TBBS.

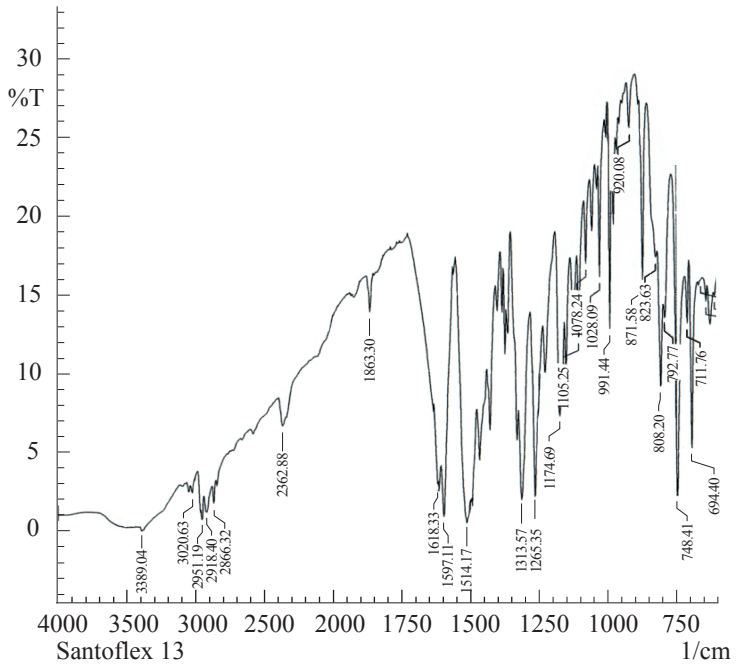

Figure 7. FT-IR spectrum of the antidegradant (Santoflex 13, 6PPD).

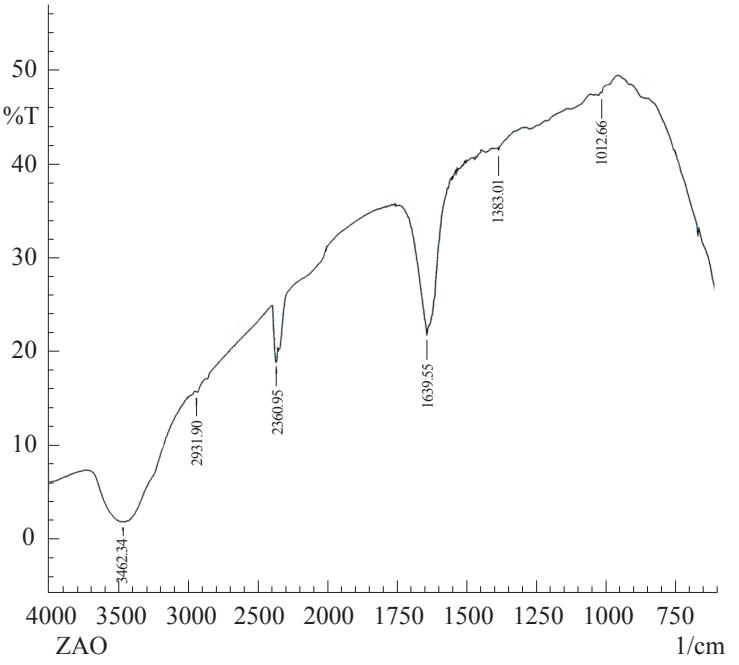

Figure 8. FT-IR spectrum of the ZnO.

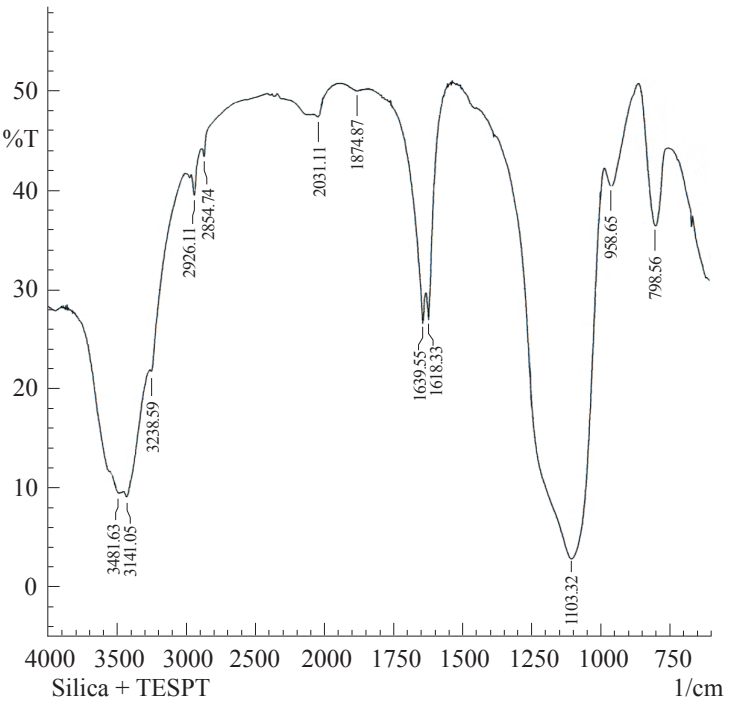

Figure 9. FT-IR spectrum of the silanised silica nanofiller.

As mentioned earlier, the melting temperature of TBBS and antidegradant were below the curing temperature of the rubber and both melted while the rubber was being cured at 140°C. When the cured bobbins were removed from the mould and cooled to ambient temperature, both TBBS and antidegradant migrated to the rubber surface at the bonded interface forming the bloom. As shown before, migration of TBBS and antidegradant damaged the rubber structure and adversely affected the surface adhesion properties of NR[7,9,10]. Thus, decrease in the durability of the bobbins (*Table 4*) and subsequent bond failure were caused by this process. It is likely that the migration of TBBS to the rubber/top-coat interface had a larger effect on the integrity of the bond than the antidegradant did and hence a shorter fatigue life for the bobbins made from compound 1. Clearly, there was an excessive amount of TBBS in compound 1 which did not react fully during the curing process and migrated to the bonded interface when the bobbins were kept in storage. For sulphenamide accelerators and phenylenediamine antidegradants, diffusion coefficients of $0.8 - 1.1 \times 10^{-7}$ cm^2/s and 1.8×10^{-7} cm^2/s at 100°C in a carbon black filled NR have been reported, respectively[22].

CONCLUSIONS

From this study, it was concluded that both compounds 1 and 2 had very low phase angles and K_d/K_s, which made them suitable for the dynamic and heat build-up applications.The bobbins failed eventually at the bond during the dynamic testing. The bobbins made from compound 1 were less durable than those made from compound 2. The migration and build-up of TBBS and antidegradant in the bonded interface between the rubber and top-coat might have caused poor adhesion and reduced the bond strength, resulting in the subsequent failure of the bobbins. It appeared that after 30 days in storage, the fatigue life of the bobbins started to deteriorate for both compounds and this was due to the damage accumulation at the bond during the dynamic fatigue tests. Compound 1 was harder and had a higher modulus and tensile strength as well as a lower elongation at break. The bobbins made from compound 1 had higher secant modulus and dynamic stiffness as well as lower phase angle and K_d/K_s but they were less durable in the fatigue test as a function of storage time. Therefore, storage of the bobbins at ambient temperature for up to 60 days was detrimental to the fatigue life of the bobbins.This was particularly so when TBBS migrated to the rubber/top-coat interface.

Date of receipt: September 2012
Date of acceptance: November 2012

ACKNOWLEDGEMENTS

The authors thank Evonik Industries AG of Germany for supplying the silica filler. The research work was partially sponsored by the University of Engineering and Technology, Lahore, Pakistan. We are also grateful to DTR VMS Limited of UK (formerly Avon Automotive VMS) for supporting this project and providing facilities for the dynamic testing of the bobbins. *Figures 6-9* were reproduced from a paper published in *J. appl. Polym. Sci.,* **124**, 1372-1383 (2012) with kind permission from Wiley Science publishers, USA.

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