



Research article

Evaluating the efficiency of functionalized zinc oxide based curing system for polychloroprene composites and analyzing its effect on curing, physical, and morphological properties for the application in specialty power transmission belts

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ABSTRACT

Polychloroprene rubber (CR) is one of the most abundantly used elastomer in power transmission belt section due to its excellent oil resistance, weather resistance, antistatic and dynamic properties. However, due to the negative impact of Zinc Oxide (ZnO) used with CR rubber towards marine environment, it is necessary to minimize the use of ZnO in CR based rubber compounds. Functionalized-ZnO(F-ZnO) being emerged as a suitable replacement for regular ZnO in rubber compounding, the effect of F-ZnO on the curing, mechanical and morphological properties of polychloroprene (CR) based composites to use in power transmission belt applications are evaluated in this work. The curing properties of F-ZnO based composites were characterized using various techniques and results were reported as a comparison with the properties of conventional ZnO (C-ZnO) based CR composites. Properties of various ZnO were analyzed using X-ray Diffraction (XRD) analysis and Field-Emission Scanning Electron Microscopy (FESEM) studies. The replacement of C-ZnO with F-ZnO help to reduce 80 % of Zn content from the end products without effecting the cure time and cross-link density of the same. 5 PHR of C-ZnO from regular compound is replaced with 1 and 3 Phr of F-ZnO and its effect on power transmission belt properties were analyzed thoroughly.

1. Introduction

From the beginning of 20th century various industries like mining and manufacturing started using power transmission belts such as V-belts for different applications [1]. The improved properties and low cost of belt drives compared to other power transmission systems leads to the wide application of belt drives in industries [2]. However, in the last few decades a sudden growth in the world-wide market for transmission belt was observed due to the rapid increase in the number of industries and need for automation [3]. So, the increased requirement of power transmission belt systems along with the special application requirements demands a continuous improvement in the belt properties in a sustainable manner to fulfil the market needs [4].

Wide varieties of power transmission belts are available in the market according to its various end uses. For most of the belt applications, heat resistance and oil resistance along with good physical properties are required due to the continuous dynamic working

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of the power transmission belts with time to time contact with oils during its application [2]. So, rubbers like Polychloroprene (CR) which is having excellent heat resistance, oil resistance, ozone resistance, and dynamic properties is a suitable candidate for such applications [5]. Most of the belts, including V-belts, serpentine, and raw edge cogged belts use chloroprene-based rubber compounds and this makes power transmission belt industries one of the main consumers of CR in the rubber market [6]. However, due to the presence of electronegative chlorine atoms next to carbon-carbon double bonds in CR, it is not curable by sulfur. To overcome this, other curing agents based on metal oxide, thiourea, and thiuram are used with CR. Usually, metal oxide-based curing is preferred for CR in industries due to its easy availability and price. For metal oxide-based curing, ZnO along with MgO is commonly used. During curing MgO prevents premature cross-linking by scavenging the excess $ZnCl_2$ formed in the system [7].

Recently, the toxic effect of Zn toward marine environment emerged as a key issue due today by day increase in the hydrocarbon waste [8]. Once the useful lifetime of rubber products is completed, it usually turned into landfill and thereafter, the excess ZnO present in the system will leach out and reach into the various aquatic systems [9]. The soluble Zn content present in these rubber products can increase the Zn concentration in waterbodies.

and once the concentration reaches its limit it become toxic and life threatening for some aquatic species [10]. As mentioned before, the improved requirement of power transmission belt systems in turn increase the hydrocarbon waste. Since, the power transmission belt industries known for its higher consumption of CR, it will also lead to the increased consumption of ZnO by these industries. To reduce the negative impact of power transmission belt industries towards the aquatic environment it is necessary to reduce the ZnO content in the rubber formulations, especially in CR based rubber compounds [11].

Usually, 5 Phr of ZnO along with 4 Phr of MgO is used as the curing system for the vulcanization of CR. Requirement of high level of ZnO addition is mainly because of the poor dispersion of ZnO inside the rubber matrix [7]. The unwanted use of ZnO in the rubber compounds can be eliminated with the benefit of nanotechnology as well as functionalization. In the recent years, a lot of research papers were published regarding the use of nano ZnO in various rubber and rubber blend-based composites. Sreethu et al. studied the efficiency of various ZnO with different surface activities on the mechanical and curing properties of the natural rubber/carbon black composites [12]. Bhowmick et al. studied the efficiency of the curing system, which is a combination of regular ZnO along with Nano MgO in CR compounds [13] Dziemidkiewicz et al. studied the efficiency of metal complexes as an ecological curing system based on heck reaction for chloroprene rubber to reduce the use of harmful chemicals [14]. Kumarjyoti et al. evaluated the efficiency of nanostructured cure activator system for polychloroprene rubber by using nano ZnO and nano MgO [7]. However, till today no evaluation was carried out on the curing efficiency of nano/functionalized ZnO based curing system in CR compounds, which is used in power transmission belt applications.

For applications like power transmission belts, high hardness, good heat ageing properties, and low compression set is required because the product is working under friction throughout its application. So, having an efficient curing system is very crucial for the better performance of power transmission belts. Therefore, the efficiency of functionalized ZnO on the curing properties of CR based power transmission belt compounds has been studied thoroughly in this work.

2. Materials and methodology

2.1. Materials

Polychloroprene rubber used for the current study purchased from Denka company limited, Japan. A sulfur modified grade (PS 40A), with a Mooney viscosity of 35 ± 5 @ ML₍₁₊₄₎ 100 °C was selected. C-ZnO was procured from Kannan Enterprises, India. The F-ZnO was purchased from Tata chemicals, India under the trade name Znmer. The properties of C-ZnO as well as F-ZnO is given in Table 1. Carbon black, FEF N 550 with a specific surface area of 42 m²/g (Method: BET) was purchased from Birla carbon, India. All the other rubber chemicals such as, Magnesium oxide, stearic acid, antioxidants, and tackifiers were purchased from Sigma Aldrich, USA. All the chemicals were used without any further modifications.

2.2. Preparation of the samples

All the rubber composites were prepared following the two-stage mixing method using a laboratory scale two roll mill, with dimensions of 150 mm × 300 mm and a friction ratio of 1:1.2. The mixing composition of different samples used for this study is given in Table 2. Two stage mixing method was followed prevent the premature curing of the samples. In the first stage, the temperature was kept around 50–60 °C and all the ingredients except curing agents were added to the masticated CR rubber and thoroughly mixed for around 7–10 min. In the second stage, curing agents were incorporated into the masterbatch at a temperature below 50 °C to prevent scorching. The mixing was kept for 3–5 min in the second stage and at the end samples were sheeted out and kept for maturation at

Table 1
Comparative properties of C-ZnO and F-ZnO.

Properties	C-ZnO	F-ZnO
Bulk Density, g/cc	0.6	0.5
Residue over #325 mesh size, %	<1	<1
Average particle size, nm (provided by supplier)	30–200	30–100
Appearance	White powder	White to off white powder

Table 2

The formulation of rubber compounds under study given in parts per hundred parts of rubber (phr).

Materials	^a C ₁₀₀ ^{CZ} ₅	^a C ₁₀₀ ^{FZ} ₁	^a C ₁₀₀ ^{FZ} ₃
Chloroprene rubber (PS40 A)	100	100	100
Polyester Flock	3.00	3.00	3.00
Magnesium Oxide	4.00	4.00	4.00
Stearic acid	1.50	1.50	1.50
Antioxidants	5.50	5.50	5.50
FEF N550	55.00	55.00	55.00
^b Processing aids	13	13	13
Regular Zinc Oxide	5.00	–	–
Functionalized ZnO	–	1	3
^c Curing agents	1.05	1.05	1.05

^a Sample designations are given according to the following: C = chloroprene rubber, CZ = regular zinc oxide, FZ = functionalized ZnO.

^b Processing aids include the following: Aromatic oil and Rubaid 16.

^c Curing agents includes Benzothiazyl Disulfide and Pre-Vulcanization Inhibitor.

ambient temperature for 24 h.

2.3. Characterization techniques

2.3.1. Characterization of regular as well as functionalized ZnO

2.3.1.1. X-ray diffraction (XRD). XRD analysis of the samples were carried using Bruker D8 Advance XRD unit. The radiation used was CuK α with a wavelength of 1.54 Å. Samples were scanned at an angular range of 10–70° 2 θ and scan rate 0.04 2 θ /s.

2.3.1.2. Fourier transform infrared spectroscopy (FTIR). FT-IR analysis of the F–ZnO and C–ZnO was carried out to find out the presence of extra functional groups present on F–ZnO compared to C–ZnO. The analysis was carried out using.

PerkinElmer FTIR Spectrometer, USA in attenuated total reflectance (ATR) mode. The measurement was carried out in the spectrum range of 4000–500 cm⁻¹ and the number of scans to record the IR spectra is 16.

2.3.1.3. Scanning Electron Microscopy (SEM). The morphology of both C–ZnO and F–ZnO was analyzed using SEM, Thermoscientific, USA. The model used was Apero-S which was operated at a voltage of 20 KV. The samples were prepared following drop-casting protocol.

2.3.2. Characterization of developed rubber samples

2.3.2.1. Curing studies. The curing properties of all the developed rubber composites were evaluated using a Moving Die Rheometer (MDR), EKT 2000s, Ektron Rheometer, Taiwan. The test was carried out for 3 min at a temperature of 180 °C. The rubber compounds were then molded with a hydraulic press referring the values obtained from the cure studies.

2.3.2.2. Mooney viscosity. Mooney viscosity of all the developed composites were studied using Mooney viscometer, MV 2000 from Alpha Technologies, Bellingham. The Mooney Viscosity of all the composites were measured under the condition ML (1 + 4) @ 100 °C, following the ASTM standard ASTM D1647.

2.3.2.3. Swelling index. The crosslink density of the rubber compounds was analyzed using swelling study. Cured rubber compounds were cut into small pieces having uniform weight(w1) and thickness (2 mm). The samples were soaked in toluene (50 ml) at room temperature for 24 h. After 24 h, the samples were taken out from toluene and wiped with tissue paper to remove excess toluene. Once the excess toluene is removed the samples weight was again measured (w2). Then the swelling index was calculated using the following equation (eq. (1)).

$$\text{Swelling Index} = \frac{\text{Final weight (w2)} - \text{Initial weight (w1)}}{\text{Initial weight (w1)}} \times 100 \quad (\text{eq. 1})$$

2.3.2.4. Cure enthalpy measurement using differential scanning calorimetry (DSC). The cure enthalpy of the developed compounds was analyzed using DSC, TA waters, USA. Cure enthalpy study can give an idea about the extent of crosslinks formed in the system during the curing process. The previously cured rubber compounds, having a weight of 100–120 mg was kept in the sample pan. The test was carried out from room temperature to 300 °C at heating rate of 20 °C/minute in an inert atmosphere (Nitrogen).

2.3.2.5. Compression set. Compression set properties gives a direct understanding about the crosslink density of the samples. The test was conducted referring the ASTM D395 standard. The specimens were prepared with dimensions of 6 mm thickness and 13 mm

diameter. The samples were prepared with a cure time of $T_{90} + 5$ min to properly cure the whole thickness of the sample. The testing was conducted at 70 °C for 70 h. The samples were compressed to 25 % of the initial thickness and the difference in thickness was measured. The compression set of the samples can be calculated following equation (2).

$$\text{Compression set (\%)} = \frac{(T_{\text{final}} - T_{\text{initial}})}{(T_{\text{initial}} - T_{\text{spacer}})} \times 100 \tag{eq2}$$

Where, T initial and T final is the initial and final thickness of the respective samples. T Spacer stands for the thickness of the spacer used for the measurement.

2.3.2.6. *Physical and heat ageing properties of the rubber composites.* According to ASTM D412, dumbbell shaped specimens were cut out from molded rubber compounds, and tensile testing was carried out using Universal Testing Machine (UTM), Instron, USA. The tests were carried out for 5 specimens from each sample and the average is reported in this paper.

Ageing properties of the vulcanizates were studied by keeping the samples in an air oven at a temperature of 100 °C for 72 h. Once the ageing is over, the sample were subjected for tensile testing. The ageing properties can be calculated following equation (3).

$$AP_{O \bullet} = \bullet^{H-O} \times 100 \tag{eq3}$$

- AP = change in tensile properties.
- H = value after ageing.
- O = original value.

2.3.2.7. *Specific gravity and hardness.* The specific gravity of the composites under study was measured using densimeter, MD 300S, Alfa mirage, Japan. The hardness of the samples was analyzed by H17A, Wallace, Digital shore a hardness tester, USA. All the values reported are an average of three tests.

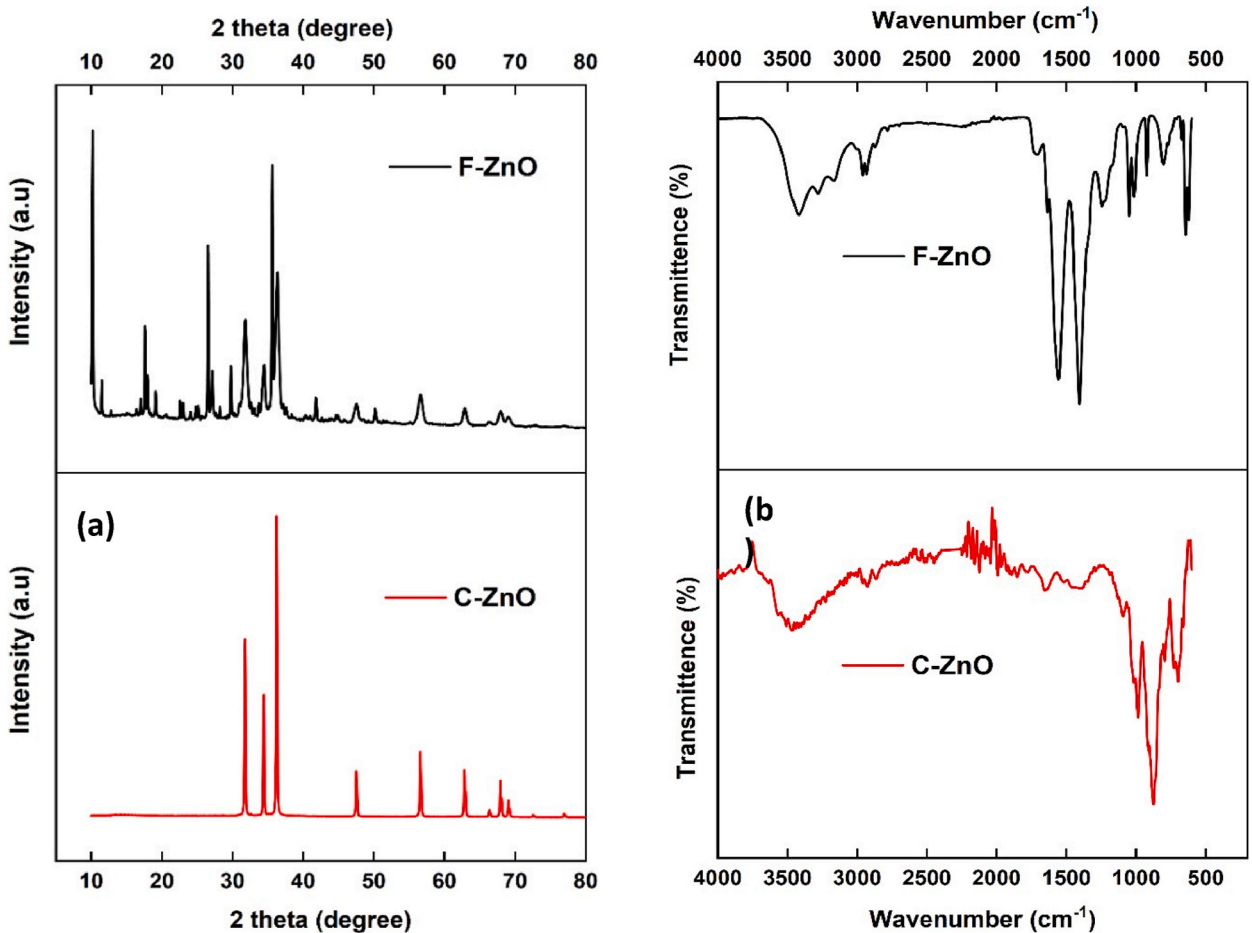


Fig. 1. Xrd spectrum for C-ZnO and F-ZnO.

2.3.2.8. Morphological analysis. The morphology of the developed composites was analyzed using Scanning Electron Microscopy (SEM) analysis. The samples were prepared by cryofracture and thereafter sputter coated with gold to make the samples conductive before analysis. The Field Emission Scanning Electron Microscope used in this study is Aperio-S, Thermo Fischer scientific with tungsten filament, USA.

2.3.2.9. Thermogravimetric analysis (TGA). TGA analysis of the rubber compounds were carried out to study the thermal degradation behavior of the developed vulcanizates. The analysis was performed using Sigma 200, TGA of TA Waters, USA following the standard ASTM D6370. The testing was conducted in a nitrogen atmosphere, at a temperature range of 25 °C–700 °C. The heating rate was kept at 20 °C/min.

2.3.2.10. Belt durability testing. The life of the belt prepared with developed nanocomposites were evaluated using flex test rigs. The belts were tested following JK Fenner, India standards which is prepared by referring BS3790:2006 standard.

3. Results and discussion

3.1. Analysis of regular and functionalized ZnO

3.1.1. X-ray diffraction (XRD) and FT-IR analysis of various nanofillers

XRD spectrum for regular as well as functionalized ZnO is given in Fig. 1(a). Both C–ZnO and F–ZnO shows the characteristic peaks of ZnO at 2 theta values of 31.65°, 34.3°, 36.14°, 47.45°, 56.43°, 62.65°, and 69.09°¹¹. The F–ZnO shows some extra peaks compared to C–ZnO, confirming the presence of extra entities in F–ZnO compared to C–ZnO. The FTIR analysis also provides the same kind of results (Fig. 1(b)), where the C–ZnO shows FTIR spectra with characteristics peaks of ZnO. However, for F–ZnO some extra peaks are present which again confirms the presence of functional groups on F–ZnO. The band present at 436 cm⁻¹ belongs to the Zn–O stretching of the ZnO lattice. In the case of F–ZnO a strong vibration is visible in between 1508 and 1378 cm⁻¹, which indicate the presence of C=O functional groups. For F–ZnO another vibration is visible at 3466 cm⁻¹ which is attributed to the presence of O–H functional groups. In the same manner the peaks at 1508 and 1378 cm⁻¹ indicate C–O and C–O–C functional groups in F–ZnO.

3.1.2. Morphology analysis of various ZnO using Scanning Electron Microscopy (SEM)

The morphology and particle size of both C–ZnO and F–ZnO was analyzed using SEM and the results are given in Fig. 2(a)&(b). From the image itself we can observe that the C–ZnO have cuboid structure. However, the F–ZnO seems to have a layered morphology than usual ZnO. The particle size of the C–ZnO and F–ZnO was measured with SEM itself. The Particle size of C–ZnO varies from 200 to 600 nm. For F–ZnO due to the agglomeration, it is difficult to identify the individual particle size. The agglomerate sizes were found out from SEM images. The F–ZnO agglomerates have an average particle size of 500–800 nm.

3.2. Characterization of developed rubber composites

3.2.1. Curing studies

The curing properties of all the developed rubber composites were analyzed and reported in the table given below. The rheographs for all the composites are given in Fig. 3. The effect of functionalized ZnO on the rheo properties of the developed composites were thoroughly evaluated by studying the curing properties such as, minimum torque (ML), maximum torque (MH), Scorch time (Ts2), and cure time (T90). The ML and MH value of the composites give an idea about the processability and crosslink density of the samples [13]. All the above mentioned properties were studied for the rubber composites and reported in Table 3. Ts2 and T90 is important during product curing because the premature curing and optimal vulcanization time required for the product is evaluated from these values [14].

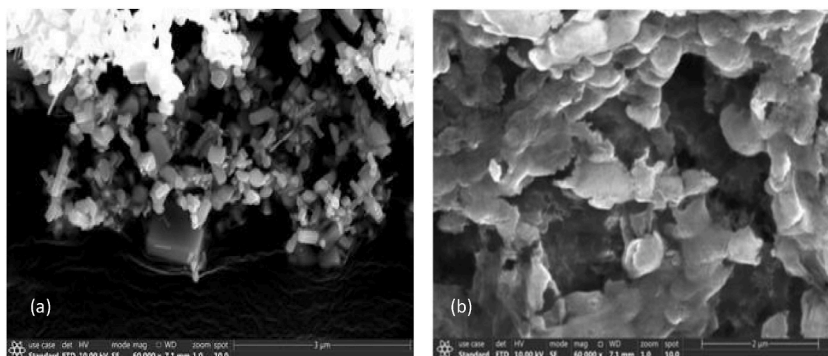


Fig. 2. The SEM images of (a) C–ZnO and (b) F–ZnO.

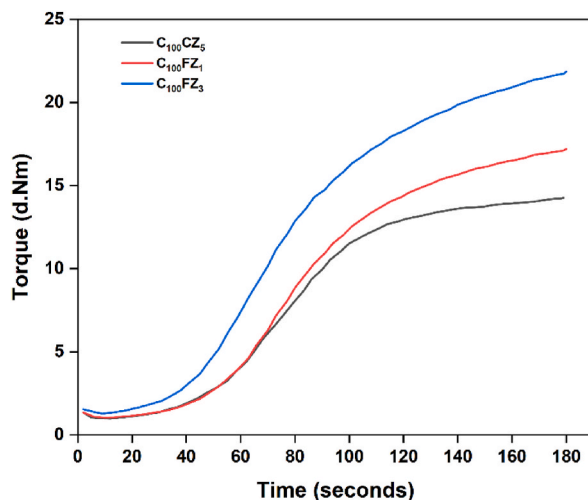


Fig. 3. The Rheographs of regular (C₁₀₀CZ₅) and developed composites (C₁₀₀FZ₁ and C₁₀₀FZ₃).

The ML value of the developed composites shows a slight increase with the addition of F–ZnO compared to the C–ZnO. This can be due to the smaller particle size of F–ZnO compared to C–ZnO which will give more reinforcing effect in the rubber composite. The effect of this increase in ML value of the developed composites can be further confirmed by studying the Mooney viscosity of the composites. The MH value gives an idea about the cross-link density in the developed composites. The addition of F–ZnO increases the MH value of the composites showing the improved efficiency of F–ZnO compared to C–ZnO. The smaller particle size and

the fine dispersion of F–ZnO in comparison with C–ZnO can be the reason for obtaining a higher MH value in the developed composites compared to the regular composites. The evaluation of scorch time of the composites is important to prevent the premature curing of the compounds during processing. The scorch time is the time required to increase two units of torque from the minimum value. The scorch time of the composites containing 5 Phr of C–ZnO and 1 phr of F–ZnO is almost similar. However, the samples with 3 Phr of F–ZnO shows a reduction in Ts2. This confirms the improved cross-link formation with the high loading of F–ZnO. Where T90 is calculated as the time required for the torque to reach 90 % of the maximum. The T90 of samples contain F–ZnO at 1 and 3 phr are same. From the results, it can conclude that the type of ZnO and its amount had no significant impact on TS2 and T90.

3.2.2. Cure efficiency by DSC study

Cure efficiency of the developed vulcanizates was identified by evaluating the observed enthalpies of compounds at a temperature range of 150 °C–200 °C [15,23,24]. When the compounds undergo time-temperature program in DSC, if it is uncured there is a chance for obtaining exotherm depending upon the elastomer, vulcanizing agents, and other ingredients used in the matrix. The DSC curves for all the developed composites are given in Fig. 4.

From the results it can be observed that the enthalpy value is gradually increasing in the order of C₁₀₀CZ₅ < C₁₀₀FZ₁ < C₁₀₀FZ₃. The results indicate that for the sample with C–ZnO the enthalpy is low, which confirms a completely cured matrix. Compared to C–ZnO samples, the samples

contain F–ZnO shows an increment in enthalpy. This may indicate the formation of cross-links at the time of DSC analysis. However, the cure enthalpy is highly affected by the type of curatives added in a particular matrix. In the case of F–ZnO may be due to the better dispersion and presence of unreacted F–ZnO in the system, some cross-link formation can happen when the samples are exposed to higher temperature. Even though, for F–ZnO based composites the enthalpy value obtained is less than one, indicate a finely cured rubber matrix. This can be further confirmed by studying the swelling behavior of the developed samples.

3.2.3. Swelling behavior

The extent of cross-links formed in a rubber matrix can be evaluated by studying the swelling behavior of particular sample in a suitable solvent. The swelling studies gives a direct idea about the amount cross-links formed in a rubber sample [16]. The swelling index of all the composites were analyzed and reported in Fig. 5. Compared to the C–ZnO, the composites containing F–ZnO shows

Table 3
The cure properties of developed rubber samples.

Samples	Minimum torque (ML), d. Nm	Maximum torque (MH), d. Nm	Torque difference (MH-ML), d.Nm	Scorch time (TS2), minute	Cure time (T90), minute	CRI _{S-1}
C ₁₀₀ CZ ₅	0.99	14.27	13.28	0.56	2.0	1.5
C ₁₀₀ FZ ₁	1.04	17.2	16.16	0.55	2.2	1.2
C ₁₀₀ FZ ₃	1.28	21.86	20.58	0.45	2.2	1.1

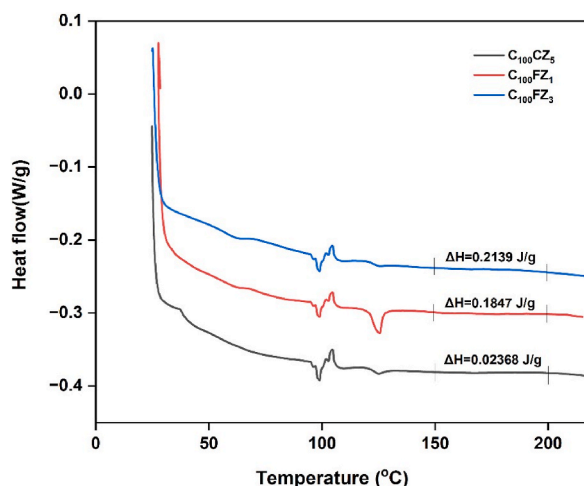


Fig. 4. DSC curves all the samples under study.

lower swelling index indicate the formation of a greater number of crosslinks in the F–ZnO based composites. Moving from 1 to 3 Phr of F–ZnO a small reduction in swelling can be noticed. This swelling behavior of the samples further confirms the better efficiency of F–ZnO towards curing compared to the C–ZnO.

3.2.4. Physical and ageing properties of the rubber composites

For applications like power transmission belts, physical properties are very much important because the products are always working under load and tension. So, the rubber compounds proposed for such applications must have good physical properties which will help to withstand extreme application conditions [11]. The physical properties of the developed composites were evaluated in terms of tensile strength (TS), elongation at break (E@B), and modulus at various strain rate (E@50 % and E@100 %). All the results are given in Fig. 6(a–c). The TS and E@B (6(a)) for compound containing 1 phr of F–ZnO shows an increment compared to C–ZnO composites. However, the sample containing 3 Phr of F–ZnO shows a slight reduction in properties compared to the regular compound. This fall in TS and E@B at higher level addition of F–ZnO can be due to the higher level of cross-links formed in the matrix, which may increase the stiffness of the matrix and leads to early failure. From the results it can be seen that the samples containing 1 phr of F–ZnO gives the properties more or less similar to the reference composites. However, the modulus @ 50 % and 100 % strain increase in an order of C₁₀₀CZ₅

<C₁₀₀FZ₁<C₁₀₀FZ₃. This can be due to the higher cross-link density possessed by the F–ZnO based composites compared to the regular compound.

After ageing, the TS and E@B of the samples were studied and reported in Fig. 6(c). Due to the metal oxide curing, even after prolonged exposure at high temperature the samples show only a slight reduction in tensile properties [10]. For TS, the change in value for C₁₀₀FZ₁ is almost similar as C₁₀₀CZ₅. For C₁₀₀FZ₃ the change is even smaller, which can be due to the higher cross-link density

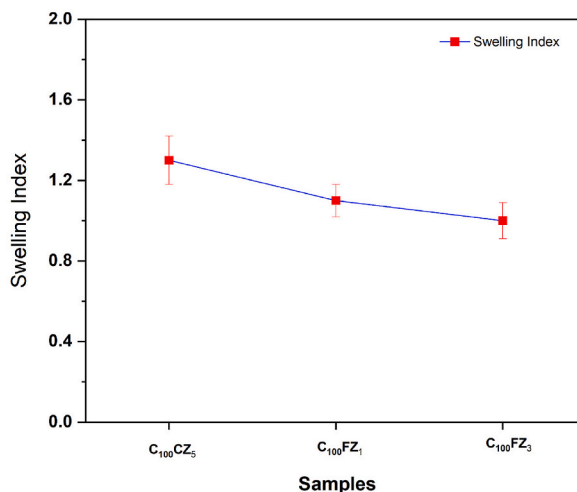


Fig. 5. Swelling Index of samples under study.

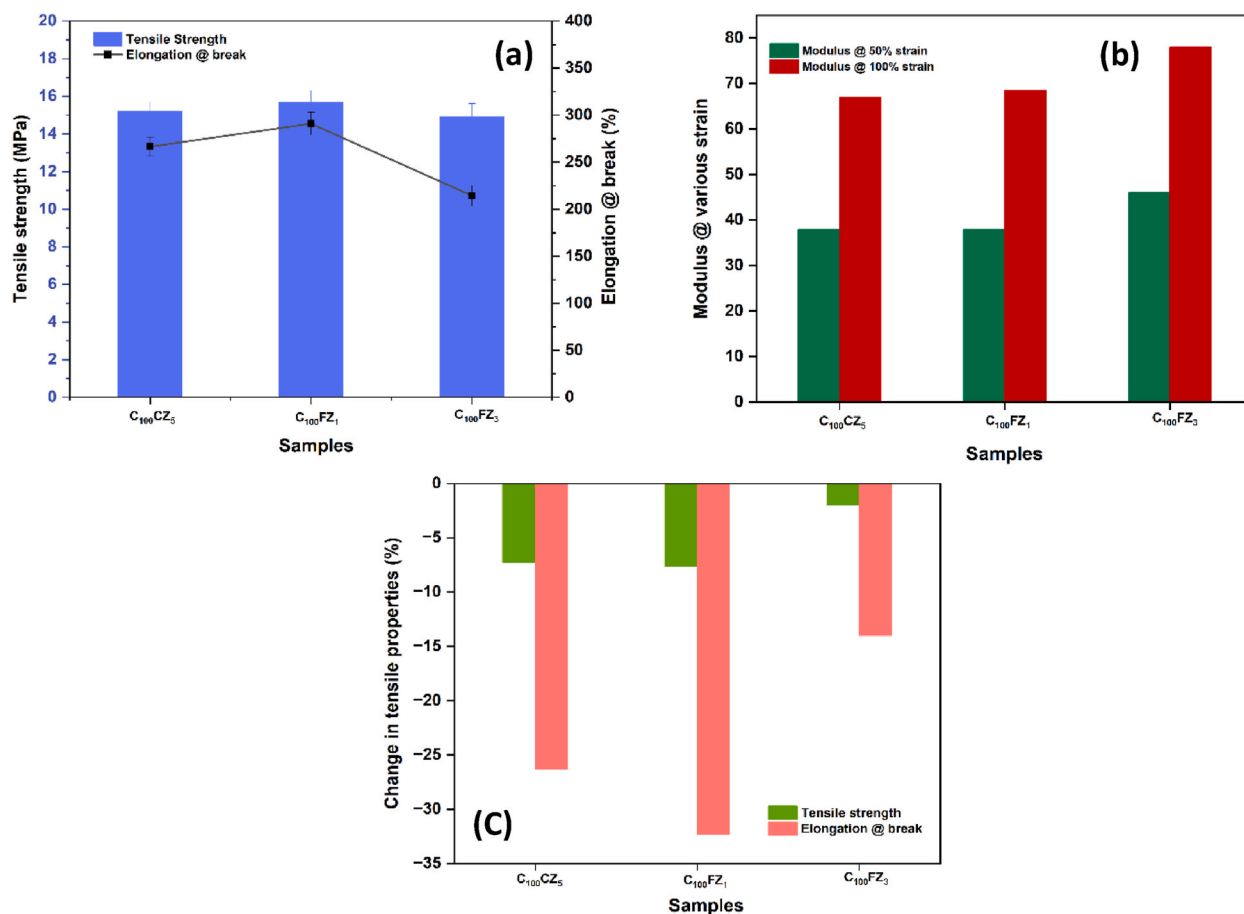


Fig. 6. Physical (a & b) and ageing (c) properties of the samples under study.

possessed by the C₁₀₀FZ₃ compared to other composites. In the case of E@B, a decrease in value after ageing is expected due to the breakage of polymer chains as well as oxidative degradation of double bonds at high temperature.

3.2.5. Compression set

While under applications, the power transmission belts will get periodically compressed in between the sides of the pulley. In order to achieve a maximum life for power transmission belts, it is necessary to have a low compression set value for subjected rubber compounds. Since the power transmission belts are working under friction, if the set value for the developed transmission belts is high it may lead to the failure of belts. So, the compression set properties of the developed composites were studied and reported in Fig. 7(a). In addition to the application-based advantages, the compression set results also gives a direct idea about the extent of cross-links formed in a rubber matrix.

From the results it is visible that, the compression set properties of the samples comes in line with the swelling behavior. The composites contain C–ZnO shows highest set value indicates lowest cross-link formation. For F–ZnO containing compounds, a reduced set value is observed indicating a higher level of cross-link formation. The improved set properties obtained for F– ZnO indicates that, the F–ZnO based developed composites are suitable and can be used in power transmission belt applications.

3.2.6. Hardness and specific gravity

The hardness and specific gravity of all the developed composites were measured and reported in Fig. 7(b). For continuous dynamic applications, such as power transmission belts a higher hardness is preferred to attain good power transmission under heavy duty conditions [17]. It is proved that the cross-link density and hardness are closely related, so the effect of F–ZnO on the hardness of the developed composites have been analyzed. From the results it can be seen that, compared to the regular compound (C₁₀₀CZ₅) the compounds containing F–ZnO (C₁₀₀FZ₁ and C₁₀₀FZ₃) have slightly high hardness values. This can be attributed by the increased cross-link density possessed by F–ZnO based compounds compared to regular one.

The specific gravity of the compounds was measured to find out the weight loss obtained through changing the curing chemicals in the formulation. Due to the high specific gravity possessed by ZnO, a small reduction in the particular material can make an impact in the overall specific gravity of the compounds [18]. With the addition of F–ZnO a slight reduction in specific gravity can be obtained

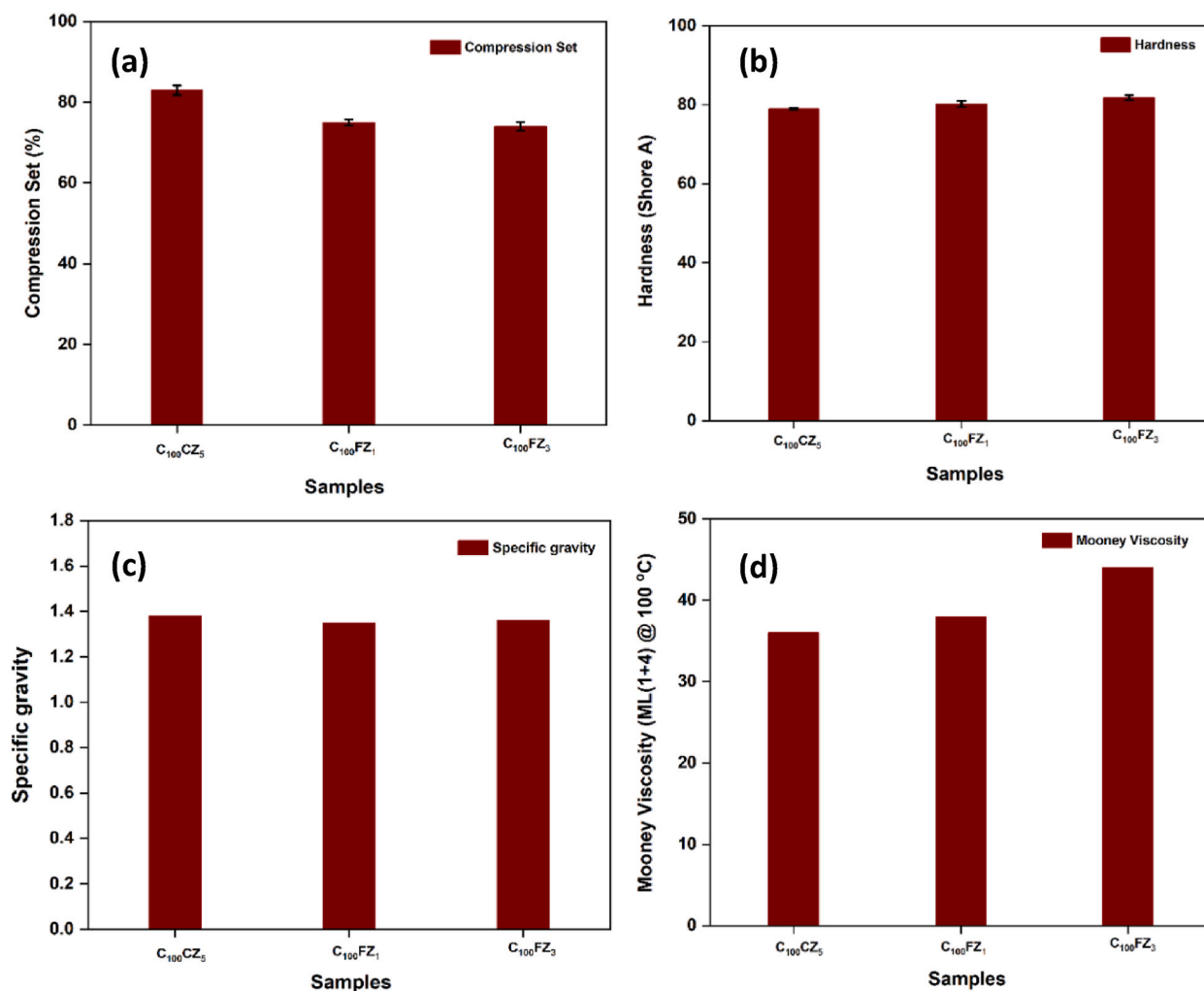


Fig. 7. (a) Compression Set, (b) Hardness, (c) Specific gravity, and (d) Mooney viscosity of the various composites under study.

from the results (Fig. 7(c)). Since, the power transmission belts are mainly used in industrial and automotive applications, reduced specific gravity can lead to limited energy consumption.

3.2.7. Processability

Mooney viscosity of all the samples were analyzed to study the processability behavior of the composites [19]. Since the ML value of the F-ZnO based composites shows an increase compared to the regular compounds it is necessary to further confirm the processability properties of the composites. The Mooney viscosity of the samples are measured and reported in Fig. 7(d). From the results it can be observed that the addition of F-ZnO into the system increases the Mooney viscosity of the composites. This can be due to the higher reinforcing efficiency of F-ZnO compared to C-ZnO. In C-ZnO based composites, due to the lower dispersion and higher particle size at 5 Phr addition itself its reinforcing effect is very less. However, for F-ZnO based composites with the addition of 1 Phr itself the Mooney viscosity has increased 5 % compared to regular C-ZnO compound.

3.2.8. Morphological analysis

The morphology of the composites developed was analyzed using SEM and the results shown in Fig. 8. The morphological analysis will help to understand the dispersion of various types of ZnO particles inside the rubber matrix.

From SEM images it is clear that compared to the regular samples, the composites containing F-ZnO shows better dispersion. The sample contain C-ZnO (Fig. 8(a)) the agglomerates are visible over the tested area. However, for F-ZnO based samples (Fig. 8(b)&(c)) no agglomerates were visible confirms the fine dispersion of F-ZnO in the matrix. The reason for the excellent dispersion of F-ZnO in the CR-matrix can be due to the presence of functional groups, which may improve the interaction between the ZnO and rubber matrix. The SEM results can further support the improved properties obtained for F-ZnO based composites in rheological and mechanical studies.

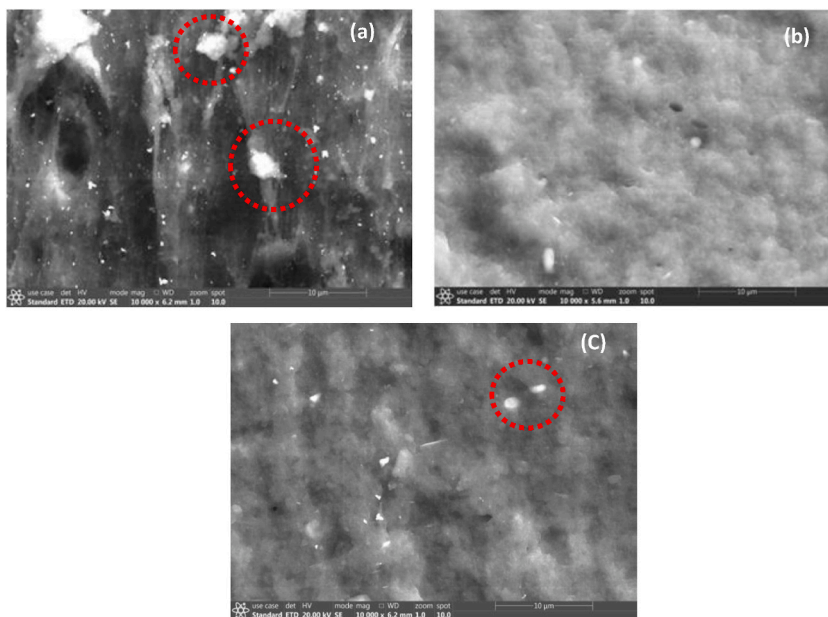


Fig. 8. The SEM images of various samples under study (a) $C_{100}CZ_5$, (b) $C_{100}FZ_1$, and (c) $C_{100}FZ_3$.

3.2.9. Thermo gravimetric analysis (TGA)

Thermogravimetric analysis of the samples was studied to find out the thermal degradation behavior of the samples. Like tire, power transmission belts are always working under dynamic application during its work-life. In addition to that, the power transmission takes place with frictional force developed between the belt and pulleys [20,21]. This may lead to the development of high temperature areas in the belts. This high temperature areas can cause failure of the belts due to thermal degradation. So, to avoid that proper study on thermal degradation behavior of developed rubber composites are required. The thermogravimograms and derivatiograms of all the developed composites were analyzed and the results are given in Fig. 9 (a) and (b) respectively.

Compared to C–ZnO based composites, the F–ZnO based shows a slight increase in initial degradation temperature. In the case of $C_{100}CZ_5$, the initial degradation (T_{95}) starts at a temperature of 277 °C. However, for $C_{100}FZ_1$ and $C_{100}FZ_3$ the T_{95} increases to 281 °C and 313 °C respectively. In the same way, the maximum degradation temperature (T_{max}) for all the composites were analyzed, for $C_{100}CZ_5$ the T_{max} was obtained as 604 °C. Whereas, for $C_{100}FZ_1$ and $C_{100}FZ_3$ the T_{max} was increased to 610 and 615 °C. This increment in T_{95} and T_{max} for F–ZnO based composites was observed due to the increased cross-link density possessed by these compounds compared to regular one [21,22].

The temperature at maximum reactive velocity (T_{mrv}) for all the composites were measured from derivatiograms (Fig. 9(b)). From the results it can be observed that, all the developed composites were having same T_{mrv} at 600 °C. The replacement of C–ZnO with F–ZnO does not have any significant effect on the T_{mrv} of the composites. However, the replacement of C–ZnO with F–ZnO does not provide any noticeable drop in degradation temperature which again confirms that the developed composite can be used for the power transmission belt applications.

3.2.10. Belt properties

Belts were prepared using the composite based on 1 phr of F–ZnO ($C_{100}FZ_1$) to compare with $C_{100}CZ_5$ based to analyze the effect of F–ZnO on the belt properties. $C_{100}FZ_1$ composite was selected because the rheological as well as physical properties of both $C_{100}CZ_5$ and $C_{100}FZ_1$ seems to be similar. However, as curing known as one of the major steps during the development of rubber products the effect of changes in the curing system on the end products needs to be evaluated thoroughly [24,25]. The belt properties were analyzed in terms of belt breaking strength and belt working hours. The properties were tested and reported in Fig. 10.

The developed belts show 20 % and 18 % increment in breaking strength and belt working life respectively from the regular compound-based belt. This can be mainly due to two reasons, the first one is higher crosslink density possessed by $C_{100}FZ_1$ and the second is higher reinforcing efficiency possessed by F–ZnO compared to C–ZnO. The improved properties of $C_{100}FZ_1$ based belts again confirms the possibility of using modified environmentally friendly compounds for power transmission belt applications.

4. Conclusions

In this study, new curing system consisting of F–ZnO instead of C–ZnO was introduced and evaluated for CR based compounds for power transmission belt applications. The C–ZnO which is using at a high Phr (5 Phr) level was replaced with lower amounts of (1 and 3 phr) of F–ZnO and its effect on the curing, mechanical, and morphological properties was analyzed. From the curing studies, it was

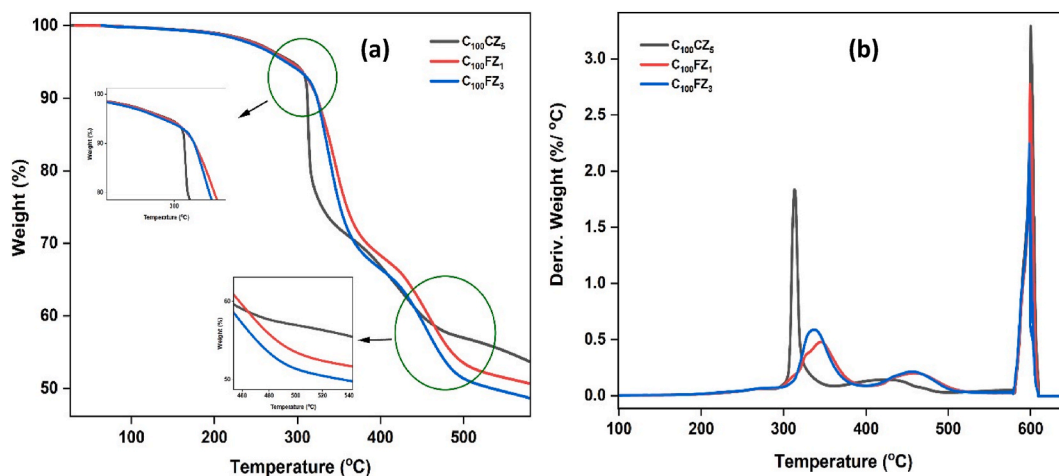


Fig. 9. (a) Thermogravimograms and (b) Derivatiograms of all the composites under the study.

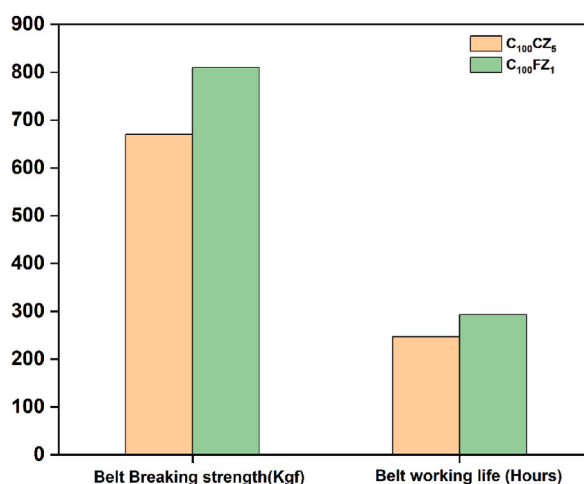


Fig. 10. Belt breaking strength and Belt working life of the developed belts From the results it can see that, by using C₁₀₀FZ₁ compound the belt properties are increasing.

found that the composite contains 1phr of F–ZnO gives better curing properties, like T₉₀, T_{s2}, and M_H values compared to the regular one. The extent of cross-links formed and the cross-link density of all the composites developed was analyzed by DSC and swelling behavior. These studies also support the curing properties. The swelling studies shows a 15–25 % reduction in swelling for F–ZnO based compounds compared to the regular one. The physical properties of the composite contain 1 phr of F–ZnO shows almost similar properties to the regular composite. However, the composite with 3 phr of F–ZnO gives improved properties in terms of modulus and thermal behavior. The morphological properties of the composites were analyzed using SEM and the results confirms an even dispersion of F–ZnO in the matrix compared to C–ZnO. Further to that, the replacement of 5phr of C–ZnO with 1 Phr of F–ZnO will also reduce 80 % of Zn content from the end products, which will be recommended due to the negative effect of Zn on the aquatic environment. So, with the introduction of F–ZnO into the curing system of CR it is possible to achieve properties same or better as the regular one with more advantage to the environment.

Data availability statement

Data will be available on request.

CRedit authorship contribution statement

T.R. Aswathy: Writing – original draft, Validation, Data curation, Conceptualization. S. Mohan: Funding acquisition. T. Kalai-vendhan: Supervision. A. Mohammed Adhil: Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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